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PYROLYSIS OF SILICON-CONTAINING CYCLIC POLYSULPHIDES

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Summary

Thermal decomposition of silicon-containing monocyclic polysulphides 1-methyl-3-trimethylsilyl-2,5-dithiacyclopentane (I), 1,4-bis(trimethylsilyl)-2,3,6,7-tetrathiacyclooctane (II) and 1-trimethylsilyl-2,3,4,5,6-pentathiacycloheptane (III)) has been studied at temperatures from 400 to 600°C using the pulse pyrolytic GC/MS method. The major decomposition of the compounds leads to trimethylvinylsilane, carbon disulphide, silicon disulphide, thiophene and its homologues as well as lower hydrocarbons and trimethylsilyl-substituted thiophenes. No similarity has been found between the electron-impact induced and thermal processes.

Introduction

Recently [1], we reported the mass spectrometric investigation of silicon-containing cyclic polysulphides and demonstrated that the compounds, containing a silicon atom in the side chain, the trimethylsilyl group, undergo extensive electron-impact promoted fragmentation to form the trimethylsilylthiirane ion-radical. Taking into account the similarity encountered between electron-impact induced fragmentation and thermal decomposition, we now investigated the gas-phase pyrolysis of 1-methyl-3-trimethylsilyl-2,5-dithiacyclopentane (I), 1,4-bis(trimethylsilyl)-2,3,6,7-tetrathiacyclooctane (II) and 1-trimethylsilyl-2,3,4,5,6-pentathiacycloheptane (III). One of the main purposes of our work was to elucidate whether silicon-containing thiiranes may be obtained from polysulphides I–III under pyrolytic conditions.

Results and discussion

Thermal decomposition of polysulphides I–III was studied by pulse pyrolytic gas chromatography/mass spectrometry (GC/MS). Reaction time was about 11–13 s.

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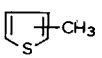
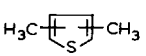
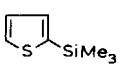
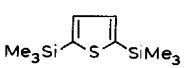
TABLE 1

COMPOSITION OF PYROLYSIS PRODUCTS (%) OF I–III AND CHARACTERISTIC IONS IN THE MASS SPECTRA OF THE IDENTIFIED COMPOUNDS

Compounds	I			II			III			Characteristic ions (m/z)
Pyrolysis products	Temperature (°C)			Temperature (°C)			Temperature (°C)			
	400	500	600	400	500	600	400	500	600	
$CH_4 + C_2H_4 + C_3H_6$	0.1	0.25	3.8	I	1	3.3	0.2	0.38	4.8	16($M^{+\cdot}$); 28($M^{+\cdot}$); 42(M^+)
$Me_3SiCH{=}CH_2$	1.8	3.8	59.2	16	17.5	30	27.6	12.8	13.8	100($M^{+\cdot}$), 85($M-CH_3$)$^+$, 73(Me_3Si^+)
COS	0.1	0.1	0.5	–	–	–	–	–	2.4	60($M^{+\cdot}$)
CS_2	0.6	1.1	15.4	1.5	6.7	11	2	18.6	67	76($M^{+\cdot}$), 44(CS^+)
 (?)	–	–	0.2	–	–	–	–	–	–	86($M^{+\cdot}$)
	–	–	0.5	–	1.0	1.0	–	0.38	0.65	84($M^{+\cdot}$), 58($M-C_2H_2$)$^+$
	–	0.1	1	–	–	–	–	–	–	98($M^{+\cdot}$), 97($M-H$)$^+$
	–	0.2	1.6	–	–	–	–	–	–	112($M^{+\cdot}$), III($M-H$)$^+$, 97($M-CH_3$)$^+$
	–	–	–	2	4.4	7	–	–	–	see Fig. 3a
	–	–	–	9.6	15.7	34	0.5	0.65	1.0	see Fig. 3b
$(Me_3Si)_2O$	1.3	1.1	1.4	2.8	3	1.5	1.7	6	5.5	147($M-CH_3$)$^+$, 73(Me_3Si^+)
$(Me_2SiO)_3$	–	0.3	0.3	–	3	1.5	–	1	4.5	207($M-CH_3$)$^+$
Conversion (%)	4	7.1	87	34	54	92	32.5	43.8	100	

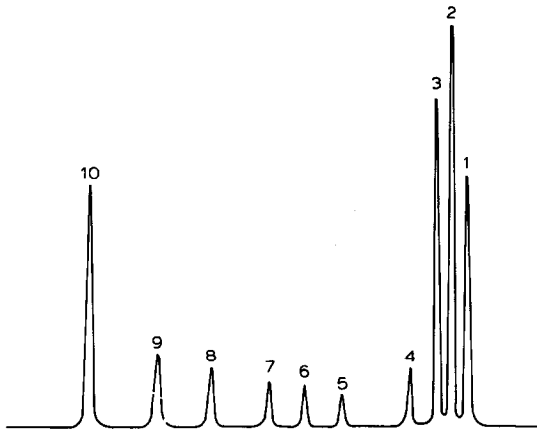


Fig. 1. Typical chromatogram of the pyrolysis products of 1-methyl-3-trimethylsilyl-2,5-dithiacyclopentane (I). 1: methane, ethylene, propylene; 2: trimethylvinylsilane; 3: carbon disulphide; 4: hexamethyldisiloxane; 5: dihydrothiophene; 6: hexamethylcyclotrisiloxane; 7: thiophene; 8: methylthiophene; 9: dimethylthiophene; 10: initial substrate I.

Separation and identification of the pyrolysis products were made by the conventional GC/MS method. Table 1 shows the compositions of the reaction mixtures obtained after pyrolysis of compounds I–III at a temperature range of 400–600°C, and the most characteristic ions in the mass spectra of the products. Typical chromatograms recorded for the pyrolysis of compounds I and II are given in Fig. 1 and 2, respectively. The chromatogram for the reaction products from III is qualitatively identical to that presented in Fig. 2. Silicon-containing thiophenes

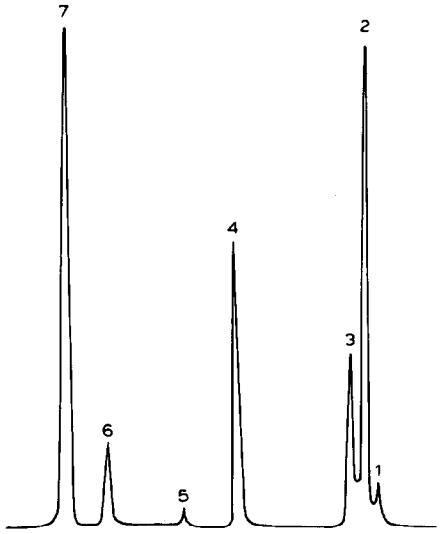
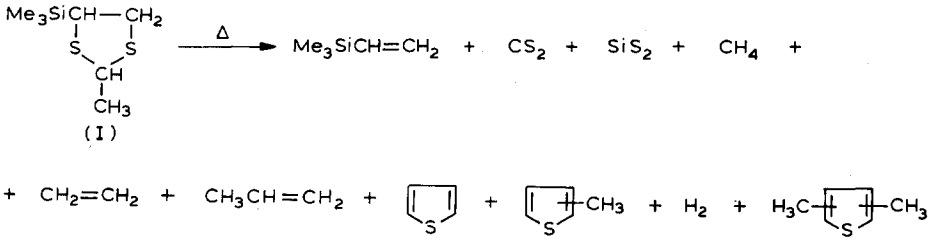


Fig. 2. Typical chromatogram of the pyrolysis products of 1,4-di(trimethylsilyl)-2,3,6,7-tetrathiacyclooctane (II). 1: methane, ethylene, propylene; 2: trimethylvinylsilane; 3: carbon disulphide; 4: benzene (solvent); 5: thiophene; 6: trimethylsilylthiophene; 7: bis(trimethylsilyl)thiophene.

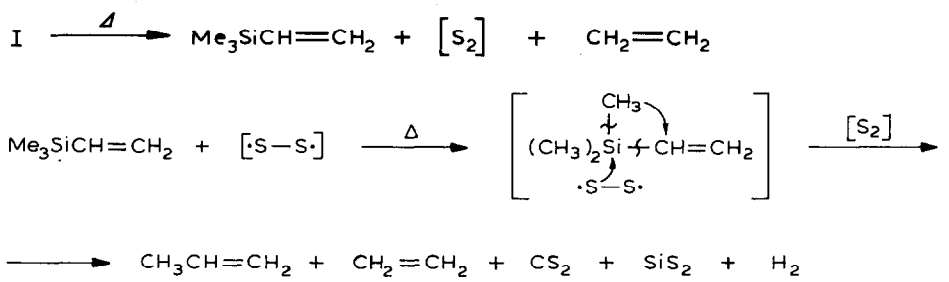
obtained during the pyrolysis of II and III were identified by comparing their mass spectra and chromatographic retention times with those of standard substances. The mass spectra of thiophenes obtained in our experiments are given in Fig. 3.

Contrary to our expectation, no similarity was discovered between the thermal and electron-impact-induced decomposition of polysulphides I–III. Thermal decomposition of these compounds starts at 400°C and is specific for each particular case.

Pyrolysis of dithiolane I results in a mixture of the following products:



Among the products, trimethylvinylsilane, carbon disulphide and methane, ethylene and propylene are the main compounds. The formation of CS_2 is probably associated both with intramolecular cleavages and with the interaction of the silane with highly reactive diatomic sulphur eliminated upon pyrolysis. The formation of propylene can be explained in terms of initial migration of a methyl radical from the Me_3Si group to the vinylic group of trimethylvinylsilane followed by scission of the $Si–C_{vinyl}$ bond, as shown below. This process is possibly promoted by the reactive S_2 molecules [2]. Simultaneous attack of S_2 molecules on the Me_2Si group of the silane is responsible for the formation of CS_2, SiS_2 and hydrogen. For complete conversion of hydrogen and lower unsaturated hydrocarbons into H_2S and CS_2, an insufficient amount of active sulphur is formed upon pyrolysis:



A similar scission of the Si–C bond accompanied by the formation of propylene has been also observed in the pyrolysis of 1-trimethylsilyl-μ_3-*S*,*S*′-ethylenedithiolatohexacarbonyldiiron [3].

The suggested mechanism is confirmed by copyrolysis of trimethylvinylsilane with S_8 at 600°C, which showed that CS_2, SiS_2 and propylene are the main products.

Copyrolysis of dithiolane I with S_8 at 600°C gives rise to only a negligible increase in an amount of CS_2 as compared with pyrolysis of I. This indicates that not only intermolecular but also intramolecular mechanisms are operative during the

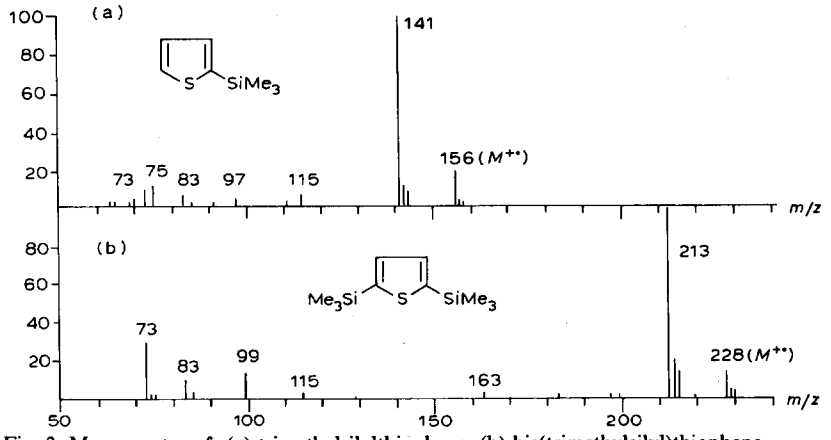
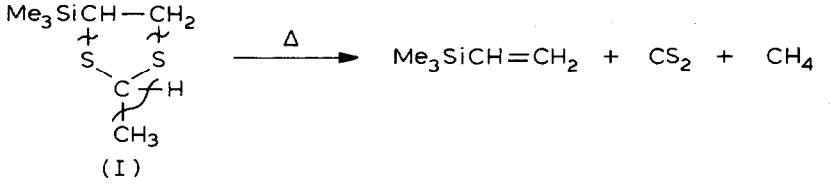


Fig. 3. Mass spectra of: (a) trimethylsilylthiophene; (b) bis(trimethylsilyl)thiophene.

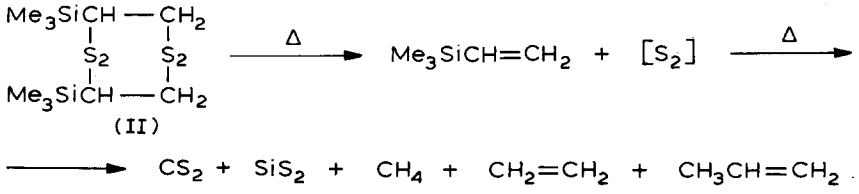
formation of CS_2 from I. However, the formation of CS_2 accompanied by intermolecular cleavage of C–S and C–C bonds, seems to be more probable:



This is underlined by the decrease in the ratio of CS_2 to $Me_3SiCH{=}CH_2$ while increasing the pyrolysis temperature. At the same time, the amount of CS_2 is increased with decreasing pyrolysis temperature of the pentasulphide III, which can only produce CS_2 due to the intermolecular interactions.

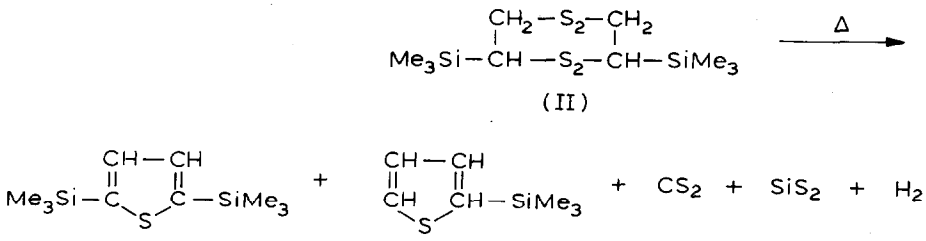
In the reaction under consideration, the appearance of thiophene and its homologues was unexpected. The thiophene may arise due to interaction of S_2 and ethylene. The formation of methylthiophene and dimethylthiophene, however, is apparently associated with intramolecular processes exclusively since no thiophene homologues were encountered among the pyrolysis products of compounds II and III.

Unlike the pyrolysis of I, cross-linked tetrasulphide II undergoes thermal decomposition in two steps. The first step involves the formation of S_2 and trimethylvinylsilane which interact further between each other to form CS_2, SiS_2 and lower hydrocarbons:



Step 1 is the dominant reaction at 400°C. It should be noted that reaction between ethylene and sulphur is responsible for the formation of a negligible amount of thiophene (see Fig. 2).

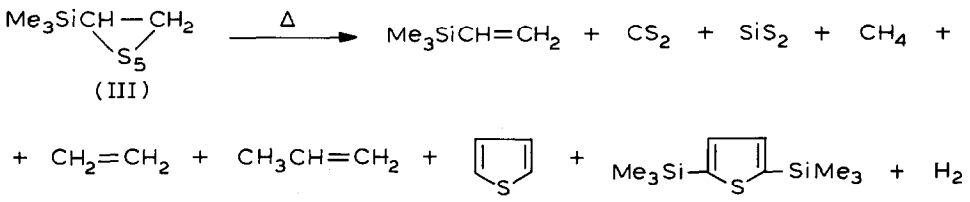
Step 2 proceeds best at 600°C and involves the loss of three sulphur atoms from the initial molecule to form trimethylsilyl-substituted thiophenes, bis(trimethylsilyl)thiophene being the main product:



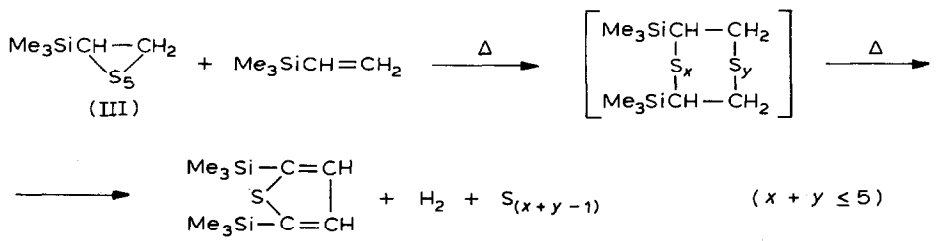
Trimethylsilylthiophene, CS_2 and SiS_2 are supposed to arise due to interaction of bis(trimethylsilyl)thiophene with active sulphur.

It should be noted that both processes, i.e. formation of trimethylvinylsilane and synthesis of silicon-substituted thiophenes, proceed with equal probability at 500°C.

Pyrolysis of cyclic pentasulphide III results in a mixture of trimethylvinylsilane, CS_2, SiS_2 and lower hydrocarbons:



At 400°C, trimethylvinylsilane is the major product. On rising the pyrolysis temperature, the amount of CS_2 is highly increased. Here, the formation of CS_2 is also due to reaction between trimethylvinylsilane and highly reactive sulphur as was the case in the thermal decomposition of dithiolane I. The presence of bis(trimethylsilyl)thiophene among the reaction products may be explained by the intermediacy of cross-linked polysulphides, which are formed from pentasulphide III and trimethylvinylsilane and decompose further to yield the silyl-substituted thiophene:



It should be noted that the formation of small amounts of siloxanes and COS during the pyrolysis of polysulphides I–III may be attributed to the presence of oxygen traces in the microreactor.

In the above discussions, SiS_2 was considered to be a product of pyrolysis. However, it was not detected by mass spectrometry. It was identified as an involatile, black coating on the inner walls of the microreactor which was readily hydrolysed by atmospheric moisture to yield H_2S.

Experimental

Syntheses and properties of polysulphides I–III were reported previously [4,5]. The thermal decomposition was performed in a quartz pulse microreactor 15 cm long and 0.6 cm in diameter in a flow of helium gas, Helium was purified from traces of water and oxygen by passing through molecular sieves and preheated copper dust. The microreactor was connected directly to the GC column of a LKB-2091 gas chromatograph/mass spectrometer. In all cases the pyrolysis time was about 11–13 s. A liquid sample of I and saturated solutions of II or III in benzene, taken in the amount of 0.1 or 0.2 μl, respectively, were introduced into the microreactor by a microsyringe through the septum.

In the chromatographic part, a stainless steel column (3 m × 3 mm) containing 10% ethylene glycole adipate coated on 150 mesh Spherochrom was used. Purified helium was used as a carrier gas with a flow rate of 20 ml/min. The oven temperature was programmed from 30 to 250°C at 5°C/min.

The mass spectra were recorded at ionizing energy 70 eV and emission current 50 μA and the temperature of the ionization chamber and of the molecular separator was 200°C.

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