Journal of Organometallic Chemistry, 402 (1991) 161–169
Elsevier Sequoia S.A., Lausanne
JOM 21162

Direct study of unstable dimethylgermathione, $Me_2Ge{=}S$, by vacuum pyrolysis-MS and low-temperature matrix IR spectroscopy

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(Received June 20th, 1990)

Abstract

Dimethylgermathione, $Me_2Ge{=}S$ (D_1), has been studied by vacuum pyrolysis-MS and matrix isolation IR spectroscopy. The germathione D_1 was generated in the gas phase by pyrolytic decomposition (730–900 °C, 10^{-2}–10^{-3} Torr) of the trimer $(Me_2GeS)_3$ (D_3) in a quartz pyrolyzer, coupled to the ionization chamber of mass spectrometer or to an optical helium cryostat, where pyrolysis products have been frozen at 12 K in an argon matrix.

The ionization energies (IE) of D_3, D_1 and its cyclodimer (D_2) have been determined from measurements of ionization efficiency curves in mass spectra of pyrolysis products of D_3 and using the semilogplot technique. The IE revealed for D_1 (8.63 ± 0.1 eV) practically coincided with that obtained earlier by PES, which proved the formation of monomeric D_1 in the reaction.

In matrix IR spectra (Ar, 12 K) of pyrolysis products of D_3 the bands at 518, 574, 606, 765, 809, 850, 1231 and 1392 cm^{-1}, disappearing simultaneously in warming-up experiments (to 35–40 K). These were ascribed to germathione D_1. By comparison of experimental frequencies with the calculated values the band 518 cm^{-1} was assigned to $Ge{=}S$ stretching vibration. The calculated $Ge{=}S$ bond force constant (4.08 mdyn/Å) is a direct physical characteristic, giving strong evidence for considerable double bonding in dimethylgermathione.

Introduction

Molecules $R_2Ge{=}X$ ($X = O, S$), containing three-coordinated germanium atom and unstable under normal conditions, are postulated as intermediates in different chemical reactions [1,2]. Information on chemical trapping of these species as well as data on quantum-chemical calculations of the simplest molecules $H_2Ge{=}O$ and $H_2Ge{=}S$ [3,4] are plentiful in current literature, but direct spectroscopic data are limited to photoelectron spectra of $Me_2Ge{=}O$ [5,6] and $Me_2Ge{=}S$ [6,7], matrix IR spectra of $R_2Ge{=}O$ ($R = F$, Me) [8,9] and X-ray data for germathione, stabilised by intramolecular complexation [10].

We report here a direct mass-spectrometric and IR-spectroscopic study of dimethylgermathione, $Me_2Ge{=}S$ (D_1), generated in the gas phase by vacuum pyrolysis of cyclotrigermathiane, $(Me_2GeS)_3$ (D_3)

$$\underset{(D_3)}{(Me_2GeS)_3} \xrightarrow{\Delta} \underset{(D_1)}{Me_2Ge{=}S} + \underset{(D_2)}{(Me_2GeS)_2}$$

A preliminary report has already been published [11].

Experimental

Parent hexamethylcyclotrigermathiane (D_3) was prepared by a published procedure [12]. The structure of a sample was verified by ^1H NMR, mass-spectra and elemental analysis.

Vacuum pyrolysis–MS study [13] of D_3 was carried out in a micropyrolyser (internal diameter 2.5 mm, length of heated zone 40 mm), coupled to the ionization chamber of an AEI MS-902 type double focusing mass spectrometer with linked scanning facilities. The solid sample of D_3 was evaporated at 70 ° C. The temperature of pyrolyzer was varied from 200 to 900 ° C. The ionization energies (IE) of D_1, D_2, D_3 and appearance energies of selected fragment ions were obtained by measuring ionization efficiency curves and using the semilog plot technique. Benzene (IE = 9.24 eV [14]) was used as internal standard.

For matrix IR spectroscopy experiments a sample of D_3, after evaporation in vacuum (10^{-2}–10^{-3} Torr, 25–90 ° C), was pyrolyzed at temperatures 490–930 ° C in a quartz reactor (inner diameter 5–8 mm, length 30–55 mm), coupled to an optical helium cryostat. The pyrolysis products were frozen at 12 K with an excess of argon (~ 1000 : 1) on the mirror copper plate, located at a distance of 50 mm from the pyrolyzer outlet. A closed-cycle refrigerator "Displex-CSW-208R" (Air Products Co.) cooled the plate. Spectra were recorded by IKS-24-LOMO IR spectrophotometer in the range 4000–400 cm^{-1} by reflection of the IR beam from the mirror plate.

Results and discussion

Mass spectrometry

Table 1 presents the main ions and their relative abundances in mass spectra of pyrolysis products of D_3 at various temperatures. Conversion of trimer D_3 at pyrolyzer temperature 820 ° C is seen to be greater than 50%. Exact mass measurements with a high resolution technique revealed (Table 1) that ions at m/z 264, 249, 132 and 117 have elemental compositions, corresponding to $D_2^{+\cdot}$, $[D_2 - Me]^+$, $D_1^{+\cdot}$ and $[D_1 - Me]^+$ respectively, independently of the temperature of pyrolysis.

The significant increase of peak intensities of these ions in step with increase of the pyrolysis temperature shows germathione D_1 and cyclodimer D_2 to be formed in the gas phase as pyrolysis products of the trimer D_3. Table 1 suggests that dimer D_2 is thermostable at 820 ° C and that it undergoes subsequent thermal decomposition to D_1 only to a limited extent. Further increase of pyrolysis temperature led to decomposition of germathione itself.

Table 1

Main ions and their relative abundances in the 70 eV mass spectra of pyrolysis products of D_3 at various temperatures.

ions	$m(^{70}Ge)/z$ [a]	relative abundances (%)		
		t_p [b] 25 °C t_k [c] 80 °C	t_p 260 °C t_k 95 °C	t_p 820 °C t_k 100 °C
$[(Me_2GeS)_3]^+ = D_3^+$	396	42.8	30.3	20.7
$D_3^+ - 15$	381	100.0	100.0	100.0
$D_3^+ - 31$	365	14.8	9.7	6.5
$D_3^+ - 47$	349	0.9	0.5	1.4
$D_3^+ - 131$	265	2.4	2.5	35.5
$[(Me_2GeS)_2]^+ = D_2^+$	264	1.9	3.2	104.6
$D_2^+ - 15$	249	113.6	107.8	460.8
$D_2^+ - 45$	219	10.5	11.0	73.3
$[Me_2GeSMe]^+$	147	6.4	6.9	48.8
$[Me_2GeSH]^+$	133	3.2	3.1	12.4
$[Me_2GeS]^+ = D_1^+$	132	1.3	1.4	19.4
$[MeGeS]^+$	117	63.6	72.3	342.4
$[Me_3Ge]^+$	115	45.5	52.0	220.3
$[Me_2GeH]^+$	101	6.4	7.8	31.8
$[Me_2Ge]^+$	100	4.1	4.6	26.7
$[MeGe]^+$	85	9.5	11.4	80.6
$[Ge]^+$	70	0.7	1.0	14.7

[a] monoisotopic mass spectra; abundances are corrected for the heavy isotopomers. [b] t_p: pyrolyzer temperature. [c] t_k: ion chamber temperature.

Our measurements of the appearance and ionization energies for some important ions are summarized in Table 2. The IE data obtained for D_1, D_2 and D_3 are very close to each other. This result is in a good agreement with the IE data obtained by photoelectron spectroscopy [6,7] and may be explained by ionization of all molecules proceeding by removal of an electron from the n_s-orbital, with very similar energies in all these molecules. The revealed ionization energy for dimethylgermatione D_1 (8.63 ± 0.1 eV) is very close indeed to the ionization energy of D_1, obtained earlier by PES (8.60 eV) [7]. This verifies the accuracy of our determination.

Table 2 shows how the appearance energies of fragment ions $[D_3 - 15]^+$ and $[D_2 - 15]^+$ exceed the appearance energies of the corresponding ions $D_2^{+\cdot}$ and $D_3^{+\cdot}$ by 0.42 eV, representing the energy necessary for cleavage of the CH_3–Ge bond.

Table 2

Energetic data obtained for $(Me_2GeS)_n$ ($n = 1$–3) and for some selected fragment ions

ions	Ionization energy IE (eV)	appearance energy AE (eV)	AE − IE (eV)
$[(Me_2GeS)_3]^{+\cdot}$	8.49 ± 0.05	–	0.42
$[(Me_2GeS)_3 - Me]^+$	–	8.91 ± 0.1	
$[(Me_2GeS)_2]^{+\cdot}$	8.63 ± 0.08	–	0.42
$[(Me_2GeS)_2 - Me]^+$	–	9.05 ± 0.1	
$[Me_2GeS]^{+\cdot}$	8.63 ± 0.1	–	–

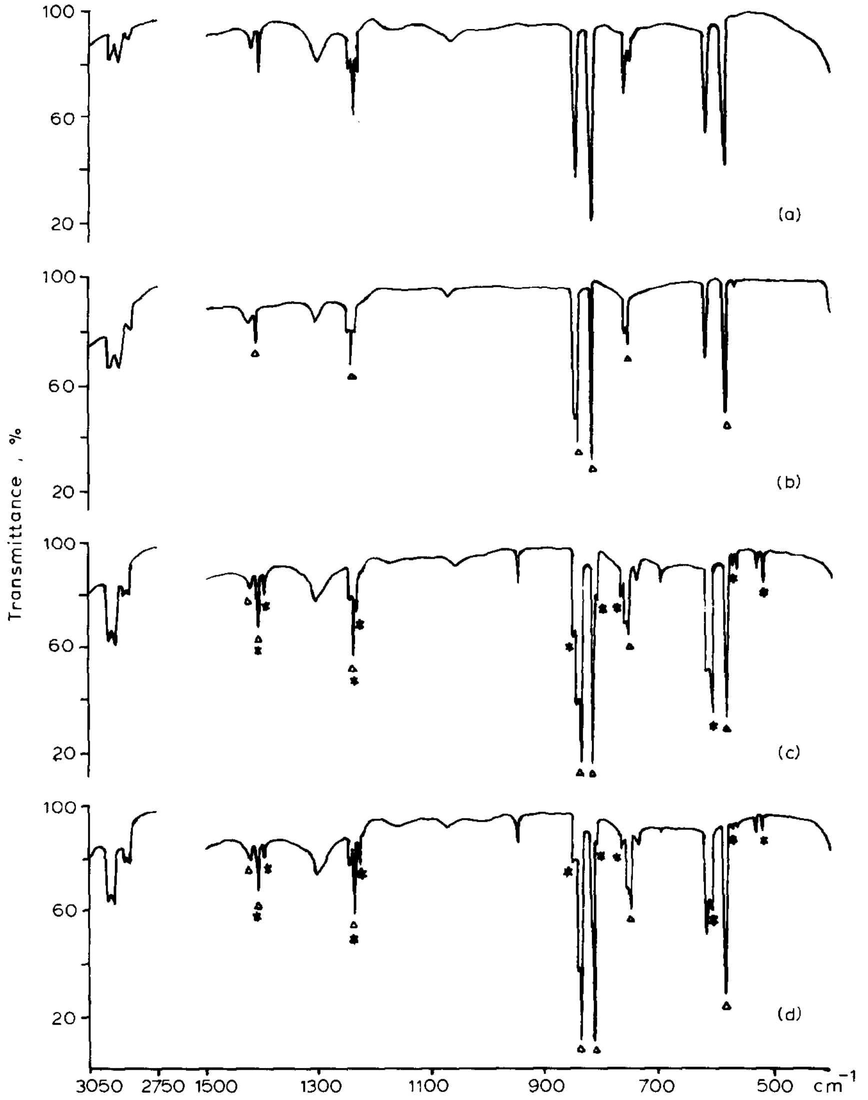

Fig. 1. (a) the IR spectrum of hexamethylcyclotrigermathiane D_3 in an Ar matrix at 12 K; (b) the IR spectrum of the pyrolysis products of D_3 (490 ° C, 10^{-3} Torr), frozen in an Ar matrix at 12 K; (c) the IR spectrum of the pyrolysis products of D_3 (930 ° C, 10^{-3} Torr), frozen in an Ar matrix at 12 K; (d) the IR spectrum of the pyrolysis products of D_3 (930 ° C, 10^{-3} Torr), frozen in an Ar matrix at 12 K, warming from 12 up to 35–40 K and recooling to 12 K. The bands of germathione D_1 are labelled by stars, the bands of cyclodimer D_2 by triangles.

Matrix isolation IR spectroscopy

The IR spectrum of $(Me_2GeS)_3$, isolated in an argon matrix at 12 K, is described (Fig. 1a and Table 3). In the spectrum of the pyrolysis products of D_3 at 490 ° C an increase has been observed of the 581, 751, 816 and 1407 cm^{-1} band intensities, compared to other bands of D_3, and a new band has appeared at 839 cm^{-1} (Fig. 1b).

Table 3

Absorption bands (cm^{-1}) of $(Me_2GeS)_3$ and $(Me_2GeS)_2$ in matrix IR spectra (Ar, 12 K)

$(Me_2GeS)_3$	$(Me_2GeS)_2$	assignment [a]
581	581	Ge–C-str.
616		
751	751	Ge–CH_3-rock.
756		
816	816	
842	839	
1233		sym. CH_3 def.
1237	1237	
1243		
1407	1407	asym. CH_3 def.
1423	1419	
2870		C–H-str.
2923		
2989		

[a] Assignment for $(Me_2GeS)_3$ have been made on base of [24]; assignment for $(Me_2GeS)_2$ have been made at the analogy of $(Me_2GeS)_3$.

With increase in pyrolysis temperature the intensities of bands at 581, 751, 816, 839, 1237 and 1407 cm^{-1} showed almost no change, while the intensities of other bands of the trimer D_3 diminished. Simultaneously the appearance of several new bands was noted.

Varying the pyrolysis temperature from 730 to 930 °C (Fig. 1b) and diluting pyrolisis products by argon, led to several groups of bands being distinguished in the 400–1500 cm^{-1} region: (i) bands of trimer D_3 at 616, 756, 842, 1233, 1243, 1423 cm^{-1} with intensities that diminished with increase of pyrolysis temperature; (ii) bands at 581, 751, 816, 839, 1419 cm^{-1} and (iii) bands at 518, 574, 606, 765, 809, 850, 1231, 1392 cm^{-1}, the ratio of whose intensities was constant in every group; (iv) bands at 531, 566, 697, 739, 822, 948, 1237 and 1407 cm^{-1}, which intensities are not proportional to the band intensities of the former three groups. It should be noted that the correlation of band intensities is conserved within group (i) and (ii) only after deducting the contribution of D_3. Besides these, bands in the 2800–3000 cm^{-1} region and bands of matrix-isolated water have been observed in the spectra of pyrolysis products of D_3.

Experiments in controlling warming of the matrix from 12 up to 35–40 K with recooling down to 12 K (Fig. 1d) revealed the following regularity. During the first warming up the matrix band intensities of group (iii) decreased synchronically, simultaneously with some diminution of bands at 1237 and 1407 cm^{-1} of group (iv), while band intensities of group (ii) increased slightly and bands of trimer D_3 conserved their intensities. Further warming up led to the disappearance of the bands of group (ii) as well as those of group (iii) and to the intensification of bands of trimer D_3. At the same time, the bands at 1237 and 1407 cm^{-1} diminished and acquired intensities, corresponding to intensities of these bands in the spectrum of trimer D_3.

Table 4

Assignment of vibrational frequencies (cm^{-1}) in spectrum of $Me_2Ge{=}S$

N	potential energy distribution (%)	$\nu_{calc.}$ (cm^{-1})	$\nu_{exp.}$ (cm^{-1})	$\nu_{exp.}$ from [17] (cm^{-1})	assignment in [17]
1	100% ν(C–H)	2973			
2	100% ν(C–H)	2973			
3	100% ν(C–H)	2973			
4	100% ν(C–H) ^{a}	2972			
5	100% ν(C–H)	2854			
6	100% ν(C–H)	2854			
7	99% α(HCH)	1382			
8	99% α(HCH)	1382	1407		
9	99% α(HCH)	1382	1392	1390	CH_3 asym. def. (in phase)
10	99% α(HCH) ^{a}	1381			
11	53% α(HCH),				
	49% β(HCGe)	1231	1237		
12	54% α(HCH),				
	50% β(HCGe)	1227	1231	1229	CH_3 def. (out-of-phase)
13	95% β(HCGe)	812	850	850	CH_3 rock. (in phase)
14	97% β(HCGe)	809	809	761	CH_3 def. (in phase)
15	97% β(HCGe)	806	765	753	CH_3 rock. (out-of-phase)
16	97% β(HCGe) ^{a}	803			
17	43% ν(Ge=S),				
	52% ν(Ge–C)	605	606	605	Ge=S stretch.
18	99% ν(Ge–C)	573	574		
19	56% ν(Ge=S),				Ge–C sym.
	35% ν(Ge–C)	518	518	516	stretch.
20	100% $\tau(CH_3)$	451			
21	100% $\tau(CH_3)$ ^{a}	444			
22	68% γ(CGeC),				
	30% γ(SGeC)	196			
23	99% γ(SGeC)	168			
24	100% $\rho(C_2GeS)$	82			

^{a} Inactive in IR.

We assigned the bands of group (iii) to dimethylgermathione D_1 (Table 4) and the bands of group (ii) to its cyclodimer D_2 (Table 3, Fig. 1b). The bands at 1237 and 1407 cm^{-1} of group (iv) probably belong to both D_1 and D_2. This conclusion allows us to explain the weakening of group (iii) bands in step with the intensification of group (ii) bands during the first warming up of the matrix by cyclodimerization of germathione D_1, while further disappearance of bands of (ii) and (iii) groups and intensification of bands of D_3 during the repeated annealing of the matrix is explained by the reaction of monomer D_1 with cyclodimer D_2, resulted in the initial trimer D_3.

The broad weak band at 566 cm^{-1}, still appearing in spectra at a pyrolysis temperature of 490 ° C, becomes intensified as the pyrolysis temperature increases and then quickly disappears upon further heating of the matrix. This band we assigned to monomeric germanium monosulfide GeS [15], which might be formed by partial thermodecomposition of germathione D_1.

The band at 948 cm^{-1}, observed in spectra at pyrolysis temperatures higher than 730 ° C, we assigned to matrix-isolated ethylene [16]. Probably, under our conditions of vacuum pyrolysis ethylene is formed on the walls of quarts reactor by secondary reactions of the methyl radical, appearing in step with GeS by thermal decomposition of germathione D_1:

$$Me_2Ge{=}S \xrightarrow{\Delta} Me^{\bullet} + GeS$$

The weak bands at 531, 697, 739 and 822 cm^{-1}, which weakened disproportionally to the bands of D_1 and D_2 while the matrix is warmed, cannot yet be definitely assigned. The identification of bands in the 2800–3000 cm^{-1} region was complicated by overlapping of vibrational bands of molecules D_1–D_3 in this range.

Our assignment of IR bands to different products of vacuum pyrolysis of D_3 is basically in agreement with independent data [17] (Table 4), though there are some differences, namely in the bands at 574, 751 (753 in [17]), 1237 and 1407 cm^{-1}. The band at 751 cm^{-1} in our opinion is not due to germathione D_1, but to its cyclodimer D_2. The bands at 574, 1237 and 1407 cm^{-1} have been assigned [17] to D_2, but our data suggest the former band belongs to D_1, and the other two bands, of group (iv), belong both to monomer D_1 and to dimer D_2. It should be also noted that the band at 809 cm^{-1} that we ascribe to D_1, was not previously observed [17].

Thus, pyrolytic mass spectrometric and matrix isolation IR spectroscopic data on composition of vacuum pyrolysis products of D_3 unambiguously show the generation of monomeric dimethylgermathione, $Me_2Ge{=}S$ (D_1), in the gas phase and its further stabilization in argon matrix at 12 K.

Vibrational assignment in the spectrum of dimethylgermathione, $Me_2Ge{=}S$. The frequency of the stretching vibration and the force constant of the Ge=S bond

For assignment of the bands to vibrational modes of dimethylgermathione molecule and for finding out the force constant of Ge=S bond we have calculated the vibrational spectrum of D_1 by force field approximation using a program package [18]. The calculation was performed for a planar model of the $Me_2Ge{=}S$ molecule, belonging to the C_{2v} symmetry group. The geometrical parameters of dimethylgermathione, necessary for calculation of cartesian coordinates, have been set in the following way. The Ge=S bond length was transferred without any change from ab initio geometry optimization of the molecule $H_2Ge{=}S$ [3]; the CGeS angle was taken to be the same as the HGeS angle in $H_2Ge{=}S$ [3]; the other geometrical parameters came from published data on the structure of Me_nGeHal_{4-n} ($n = 3, 4$) [19].

The initial force field for the first approximation of the vibrational frequencies of D_1 was chosen on the basis of the known force fields of molecules Me_nGeHal_{4-n} ($n = 3, 4$) [19] and GeS [15]. To match experimental and calculated spectra the force field of D_1 was varied during the next steps of calculation, leading to the vibrational spectrum of $Me_2Ge{=}S$ shown in Table 4.

The obtained potential energy distribution, shows the Ge=S stretching vibration not to be characteristic for the molecule D_1. This vibration interferes markedly with symmetrical Ge–C vibration, resulting in two frequencies (606 and 518 cm^{-1}), with the greatest contribution of ν(Ge=S) vibration being to the latter frequency.

Vibration frequencies of bonds C=O, Si=O and Ge=O in the spectra of CO, SiO [20] and GeO [21] are always located higher than in the spectra of respectively $Me_2C{=}O$, $Me_2Si{=}O$ [22,23] and $Me_2Ge{=}O$ [9]. That the monomeric GeS molecule absorbs in the IR spectrum at 566 cm^{-1} [15], suggests that ν(Ge=S) vibration would

Table 5

The calculated force field for $Me_2Ge{=}S$

N	Force constant	The value of force constant
1	$F(\nu(Ge{=}S))$	4.081 mdyn/Å
2	$F(\nu(Ge{-}C))$	2.550 mdyn/Å
3	$F(\nu(C{-}H))$	4.700 mdyn/Å
4	$F(\gamma(CGeC))$	0.430 mdyn·Å/rad^2
5	$F(\gamma(CGeS))$	0.380 mdyn·Å/rad^2
6	$F(\alpha(HCH))$	0.492 mdyn·Å/rad^2
7	$F(\beta(HCGe))$	0.440 mdyn·Å/rad^2
8	$F(\tau(CH_3))$	0.370 mdyn·Å/rad^2
9	$F(\rho(C_2GeS))$	0.070 mdyn·Å/rad^2
10	$f(\alpha(HCH), \beta(HCGe))$	0.022 mdyn/rad
11	$f(\nu(Ge{-}C), \nu(Ge{-}C))$	0.162 mdyn/rad
12	$f(\nu(Ge{-}C), \nu(Ge{=}S))$	0.096 mdyn/ rad

be seen in spectrum of $Me_2Ge{=}S$ in the lower frequency range. In this connection, we consider the assignment of the frequency at 518 cm^{-1} to $\nu(Ge{=}S)$ vibration more reasonable than the assignment [17] of frequency at 605 cm^{-1} to this vibration.

The force field, which permitted best agreement of experimental and calculated frequencies, is given in Table 5. The calculated value of Ge=S bond force constant $F(\nu(Ge{=}S))$ is 4.08 mdyn/Å which is very close to the value for the double bond in the GeS molecule (4.22 mdyn/Å [15]). This physical characteristic represents strong evidence for a considerable double bonding between germanium and sulphur atoms in the molecule of dimethylgermathione.

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