Matrix Isolation and IR Spectroscopy of Germanethione $Me_2Ge{=}S$

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Received February 27, 1989

The matrix isolation technique permitted the trapping and IR identification of dimethylgermanethione, Me_2GeS, formed either by gas-phase pyrolysis of $(Me_2GeS)_3$ or by interaction between sulfur atoms and dimethylgermylene.

During the last years there has been much interest in the chemistry of unsaturated organometallic compounds $R_2M{=}X$ (M from group 14, X = O, S).[2–10] Reports of chemical trapping of these short-lived intermediates are numerous, but there exist few spectroscopic data on this family: mass spectrometry for $R_2M{=}S$ (M = Ge,[11] Si[12]), infrared spectroscopy for $R_2Si{=}O$,[13–16] and photoelectron spectroscopy for $R_2Ge{=}X$ (X = O, S)[17–19] and $R_2Si{=}S$.[17] We wish to report the first matrix isolation and IR spectrum of a germanethione, $R_2Ge{=}S$. There is some chemical trapping evidence[3,6,20–30] for the existence of dimethylgermanethione, $Me_2Ge{=}S$ (**1**), as a transient species (Chart I), but to date the only proof of its occurrence in free state is UV photoelectron spectroscopy.[17]

Table I. Vibrations of Dimethylgermanethione (1)

mode	symmetry	calcd^a	obsd^b	assignmt
ν_1	a_1	2938 (26)		CH_3 sym stretch (in-phase)
ν_2		2822 (4)		CH_3 sym stretch (in-phase)
ν_3		1389 (6)		CH_3 sym def (in-phase)
ν_4		1247 (28)		CH_3 def (in-phase)
ν_5		811 (74)	850 (s)	CH_3 rock (in-phase)
ν_6		599 (72)	605 (vs)	Ge=S stretch^c
ν_7		510 (10)	516 (m)	GeC sym stretch^c
ν_8		173 (2)		C–Ge–C scissor
ν_9	a_2	2908 (0)		CH_2 asym stretch (out-of-phase)
ν_{10}		1391 (0)		CH_3 asym def (out-of-phase)
ν_{11}		695 (0)		CH_3 def (out-of-phase)
ν_{12}		46 (0)		CH_3 rotation (out-of-phase)
ν_{13}	b_1	2910 (23)		CH_2 asym stretch (in-phase)
ν_{14}		1401 (22)	1390 (m)	CH_3 asym def (in-phase)
ν_{15}		741 (19)	761 (m)	CH_3 def (in-phase)
ν_{16}		161 (4)		out-of-phase "umbrella" bend
ν_{17}		56 (0)		CH_3 rotation (in-phase)
ν_{18}	b_2	2937 (19)		CH stretch (out-of-phase)
ν_{19}		2820 (6)		CH_3 sym stretch (out-of-phase)
ν_{20}		1378 (5)		CH_3 sym def (out-of-phase)
ν_{21}		1242 (46)	1229 (m)	CH_3 def (out-of-phase)
ν_{22}		732 (26)	753 (m)	CH_3 rock (out-of-phase)
ν_{23}		590 (38)		GeC asym stretch
ν_{24}		161 (13)		C–Ge–C rock

^{a} Hartree–Fock calculation with DZ+d basis set. All calculated frequencies were multiplied by 0.9 to correct at least in part from the known inadequacy of the HF model. Frequency in units of cm^{-1}; intensity in parentheses in km/mol. ^{b} In units of cm^{-1}. ^{c} The Ge=S and the symmetric Ge–C stretches are strongly mixed.

Experimental Part

The matrices were prepared by using standard vacuum-line techniques and a Displex 202E cryostat (Air Products Co.). They were formed on a cold (18–20 K) CsI window by condensing a

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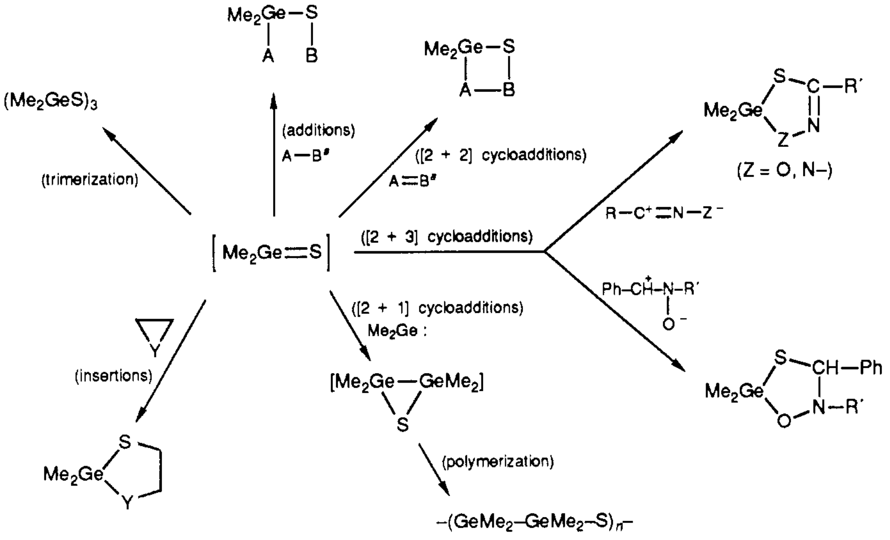
Chart I. Reactivity of Dimethylgermanethione



[a] A-B = YGeR′$_3$ (Y = OR, SR), Y-GeR$_2$ (Y = O, S). A=B = >C=O, >C=S, >C=N-, >Ge=CH$_2$.

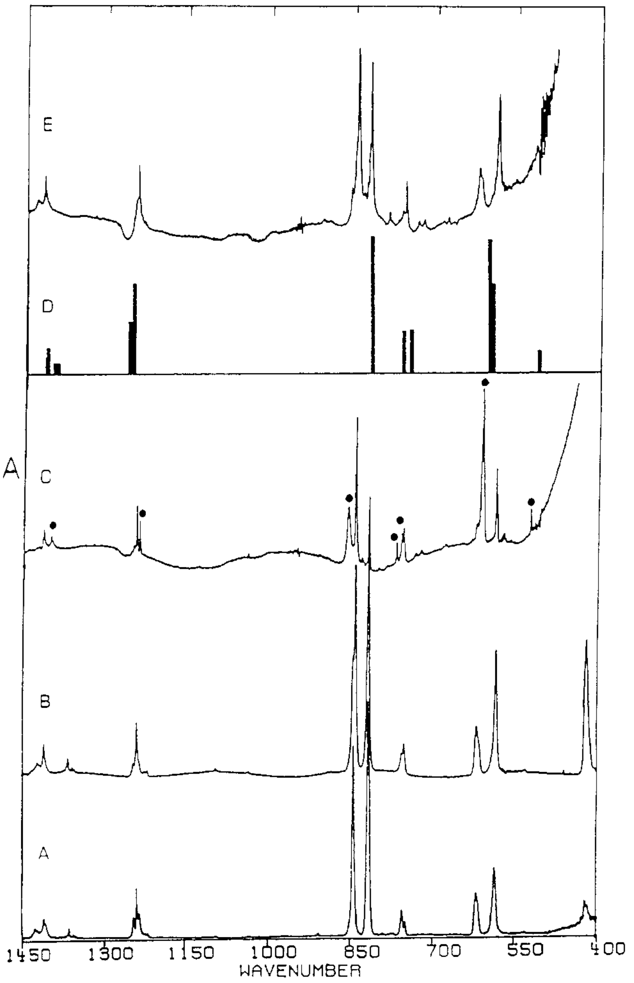


Figure 1. Argon matrix isolation (17–18 K) IR spectra of (Me$_2$GeS)$_3$ (A) and products of (Me$_2$GeS)$_3$ pyrolyzed at 450 °C (B) and at 650 °C (C). The seven new bands attributed to 1 are marked with black dots. The spectrum E was recorded after sample C was annealed at 46 K. The bar diagram shown in D represents the ab initio calculated IR spectrum of 1 (see text and Table I).

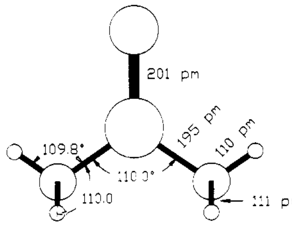


Figure 2. Calculated equilibrium geometry of 1 (HF/DZ+d).

stream of argon and vapor of 2 from a furnace constructed of either quartz or boron nitride. The spectra were recorded by using a Nicolet 60-SXR FT-IR spectrometer. The samples of 2 and 3 were prepared by using published procedures.[17,22] GC–MS analysis was performed by using a Model 5995 Hewlett-Packard instrument.

Calculations

Ab initio calculations of frequencies and intensities in the harmonic approximation were performed on an X-MP/24 computer at the University of Texas, at the Hartree–Fock level, using the gradient method and the GAUSSIAN 86[31] computer program. All calculations were carried out with a DZ+d basis set.[32]

Results and Discussion

The trimer (Me$_2$GeS)$_3$ (2) is known to be a convenient thermal source for 1.[17,22] In order to obtain this highly reactive compound in argon matrix isolation, 2 was subjected to flash pyrolysis in a stream of argon and quenched on a cold window. The resulting matrix IR spectra are shown in Figure 1.

According to results obtained by UV photoelectron monitoring,[17] the vacuum pyrolysis of 2 proceeds at temperatures above 300 °C (5×10^{-2} Torr). In the IR spectra of the matrix-isolated products from a vapor of 2 heated to temperatures just above 300 °C, we observed new IR bands (Figure 1B). Their intensity increased considerably when the pyrolysis temperature was raised to 550 °C. Their positions are very close to the characteristic bands

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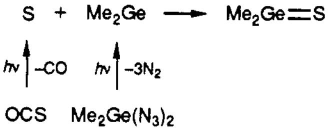
of **2**. According to mass spectra obtained under these conditions[11] we believe that these bands are due to the cyclic dimer of **1**, $(Me_2GeS)_2$ (**3**). This was indeed detected by GC–MS after warmup. The same close correspondence is known to exist between the IR spectra of the isolated silicon analogues $(Me_2SiS)_3$ and $(Me_2SiS)_2$.[33]

When **2** was flash pyrolyzed at 650 °C (10^{-4} Torr) in Ar, a set of seven new bands was observed at positions listed in Table I, in addition to those of **3** and to a series of very weak closely spaced bands attributable to the isotopic species of GeS[34] (Figure 2C). When the matrix was warmed from 18 K to annealing temperatures (35–45 K, Figure 2E), the seven new bands disappeared simultaneously, suggesting that they all belong to the same unstable species. At the same time, peaks due to **3** increased in intensity. The new bands were not associated with any distinct absorption bands in the visible region.

A further increase of the pyrolysis temperature caused a reduction of the intensity with which the seven new bands appear and an increase in the intensity of the peaks attributed to GeS, $CH_3^\bullet$,[35] C_2H_2, and CH_4. Upon deposition of the reaction products through an oven held at 650 °C without argon, only **3** was observed in the IR spectrum as would be expected in the absence of isolation. In light of these results, it would appear that the seven new bands are due to dimethylgermanethione **1**. We propose that it dimerizes readily to yield **3** already at very low temperatures and also that it is unstable with respect to decomposition into GeS and $CH_3^\bullet$ at temperatures higher than about 700 °C:

$$Me_2Ge{=}S \xrightarrow{\Delta} 2Me^\bullet + GeS$$

Supporting evidence for this structural assignment was obtained in an IR study of photolysis of dilute argon matrices containing OCS and $Me_2Ge(N_3)_2$ (**4**) codeposited on a CsI window (17 K). After irradiation with a low-pressure mercury lamp, the IR spectrum showed the same seven new bands, consistent with the expected formation of **1** by reaction between sulfur atoms and dimethylgermylene obtained by photodecomposition of OCS[36] and $Me_2Ge(N_3)_2$,[37] respectively.



$$\begin{tikzcd} \mathrm{S} & + & \mathrm{Me_2Ge} \arrow[r] & \mathrm{Me_2Ge{=}S} \\ \mathrm{OCS} \arrow[u, "h\nu"', "-\mathrm{CO}"] & & \mathrm{Me_2Ge(N_3)_2} \arrow[u, "h\nu"', "-3\mathrm{N_2}"] & \end{tikzcd}$$

Finally, confirming evidence for the assignment of the seven new bands to **1** was obtained by comparison of their frequencies and relative intensities with those calculated at the ab initio Hartree–Fock level. The computed spectrum, incorporating an empirical 90% scaling correction for the frequencies, is shown in Figure 1, part D, and the agreement with the experimental spectrum shown in Figure 1, part C, is seen to be excellent. All of the experimental bands are accounted for well, and all of the computed intense bands are observed at the right locations.

The computational results, listed in Table I, also suggest detailed assignments of the nature of the motions involved in the individual normal modes. It is reassuring that they all correspond to motions one would have guessed from the molecular structure anyway.

The vibration that is of most interest is the Ge=S stretch at 604.5 cm^{-1}. It is quite intense, as expected for the stretching vibration of a highly polar bond. A shoulder on the high-frequency side has a fairly complex structure. Some of it may be due to isotopic splitting, some is undoubtedly due to **2** and **3**, some may be due to a methyl radical byproduct (603[38]–612[35] cm^{-1}), but some could well be due to the Ge–C asymmetric stretch vibration, calculated to occur in this region with fair relative intensity. The value calculated for the Ge=S stretch in **1**, 666 cm^{-1} before the scaling correction, can be compared with the uncorrected value of 586 cm^{-1} computed previously[39] for $H_2Ge{=}S$.

According to our calculation, the Ge=S stretching motion dominates this mode but is mixed to a degree with a symmetric Ge—C stretch. The rather high frequency of the Ge=S stretch suggests a fair degree of double-bond character in this polar bond; single-bond Ge—S stretching vibrations normally occur near 410 cm^{-1}.[40–43]

The calculated equilibrium geometry is of C_{2v} symmetry (Figure 2). The computed Ge=S bond length in **1** is 201 pm, not very different from that calculated in $H_2Ge{=}S$ (202 pm[39]) and identical with that found in GeS (201 pm[44]) but substantially shorter than a standard single Ge–S bond (222 pm).[41] The computed Ge–C bond lengths in **1** are 195 pm and the C–Ge–C angle is 110.0°. The computed dipole moment is 4.6 D.

In summary, the IR spectra and the calculations agree that the Ge=S bond in **1** is a highly polar true double bond.

Acknowledgment. This work was supported by an AFOSR contract (87-0001B) and by a grant of computer time from the University of Texas.

Registry No. **1**, 16090-49-6; **2**, 16090-54-3; **3**, 121192-28-7; **4**, 20588-37-8; OCS, 463-58-1; Me_2Ge, 74963-95-4; S, 7704-34-9.

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