Vacuum Pyrolysis−Matrix Isolation FTIR and Density Functional Theoretical Studies of Transient Dimethylgermanone, $(CH_3)_2Ge{=}O$

Valery N. Khabashesku,* Sergei E. Boganov, Konstantin N. Kudin, John L. Margrave, and Oleg M. Nefedov

Department of Chemistry, Rice University, Houston, Texas 77005-1892, and the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leniskii prospekt, Moscow 117913, Russian Federation

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The transient organic germanone $(CH_3)_2Ge{=}O$ (**1**) was generated by vacuum pyrolysis from three precursors, 3,3-dimethyl-6-oxa-3-germabicyclo[3.1.0]hexane (**2**) and its 1,3,3,5-tetramethyl analogue (**3**) and octamethylcyclotetragermoxane (**4**), and directly observed in argon cryogenic solid matrixes at 12 K by FTIR spectroscopy. The unstable dimer of **1**—tetramethyl-1,3-cyclodigermoxane (**6**)—has been tentatively identified in the spectra of matrix-isolated pyrolysis products from **2**−**4**. The production of the transient germene $(CH_3)_2Ge{=}CH_2$ (**9**) and acrolein from **2** and of isopropenyl methyl ketone from **3** have also been observed, providing evidence for a new route of the thermal decomposition of epoxides **2** and **3**. Vibrational assignments of the spectral bands, attributed to germanone **1** and its cyclodimer **6**, have been done by comparison with the density functional theory B3LYP/6-311G(d,p) calculated harmonic frequencies and infrared intensities, assisted by vibration visualization and calculations of potential energy distributions (PED) for each normal mode. The excellent agreement between the experimental and calculated frequencies and the observation of isotopic splittings of the Ge=O and Ge−C stretching fundamentals due to natural abundances of germanium, being in accord with the computed isotopic shifts, provide firm evidence for the structural identification of germanone **1**. The observed frequency and the calculated force constant and bond order of the Ge=O moiety in **1** are found to be lower than those in the parent germanone $H_2Ge{=}O$ (**5**) and in $F_2Ge{=}O$. These studies correct the assignment of the Ge=O stretching frequency in **1** given earlier in our preliminary report.

Introduction

The germanium analogues of ketones, $R_2Ge{=}O$ (germanones), are very reactive molecules of substantial synthetic, mechanistic, and theoretical interest.[1] Unlike their relatives with Ge=S double bonds, which have recently been isolated and studied by X-ray diffraction as monomers due to stabilization by either intramolecular base complexation[2] or steric hindrance from diaryl substituents,[3a] the germanones are known so far exclusively as transient species in spite of the ongoing attempts to stabilize them kinetically by heavy substituents.[3b] They readily undergo oligomerization and addition reactions[1] influenced by the strong polarization of the Ge=O bond, which according to the calculations is suggested to be intermediate between π and semipolar chemical bonds.[4,5] The trimerization of the parent germanone $H_2Ge{=}O$ into $(H_2GeO)_3$ was calculated to be exothermic by about 55 kcal/mol.[5] The theoretical studies also predicted a lower thermodynamic stability for $H_2Ge{=}O$ with respect to the cis and trans germylene HGeOH isomers by 18 kcal/mol[4] or, according to the latest computation, by about 30 kcal/mol.[5] The dimethyl substitution notably stabilizes the germanone structure, which, although remaining less favored than the cis and trans CH_3GeOCH_3 isomers, reduces the energy difference to only 5−7 (MP4), 9−11 (CCSD/T) or 10−12 (B3LYP) kcal/mol.[5] Thus, the intermolecular oligomerization reactions to cyclic germoxanes and probably, to some extent, the intramolecular rearrangement into germylene isomers are likely to present the main obstacles for observation of free germanones. Only very few from this family have been directly characterized by spectroscopic methods. The inorganic germanones $F_2Ge{=}O$, $H_2Ge{=}O$, and $(HO)_2Ge{=}O$ as well as $O{=}Ge{=}O$ molecules were in situ photochemically generated in solid inert matrixes, and their IR absorptions have been

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reported.[6-8] The vapor-phase GeO monomer has been produced at high temperatures and trapped in nitrogen and argon matrixes.[9-11]

The direct physicochemical studies of organic germanones are limited, so far, to dimethylgermanone, $(CH_3)_2Ge{=}O$ (**1**). PES studies[12] have shown that **1** has a very short lifetime in the gas phase at temperatures higher than 150 °C and recombines with the formation of the stable cyclotrimer $(Me_2GeO)_3$. The preliminary results of the IR investigation of matrix-isolated **1** have been reported.[13] In the present paper we provide a full description of the latter work as well as new and corrected infrared data on **1** obtained after reinvestigation of the precursors for **1** and their decomposition products with the help of higher resolution FTIR spectroscopy.

The germanone **1** was generated by vacuum pyrolysis of 3,3-dimethyl-6-oxa-3-germabicyclo[3.1.0]hexane (**2**) and its 1,3,3,5-tetramethyl analogue (**3**) and the cyclic tetramer of **1**$-(Me_2GeO)_4$ (**4**). The compounds **2**−**4** were chosen as precursors for **1** on the basis of known chemical trapping studies and the composition of final products of their pyrolyses, suggesting the intermediacy of **1**.[14,15] This choice was also made in view of proven successful utilization of the silicon analogues of **2**−**4** in the gas-phase generation and matrix isolation of dimethylsilanone, $Me_2Si{=}O$, which led to observation of the most intense IR spectrum of this transient molecule so far.[16]

Experimental Section and Calculations

General Methods. ^1H and ^{13}C NMR spectra of **2**−**4** were recorded on Bruker WM-250 and AM-300 spectrometers. Mass spectral analyses were performed on a Varian MAT 311 and AEI MS 902 instruments at 70 eV ionization energy. GC-MS analyses were done on a Finigan MAT Incos 50 spectrometer using an RSL-200 capillary column (0.25 mm × 30 m).

Materials. 3,3-Dimethyl-3-germa-6-oxabicyclo[3.1.0]-hexane (2). The precursor **2** was synthesized according to a previously described procedure[17] by the reaction of *p*-(methoxycarbonyl)perbenzoic acid with 1,1-dimethyl-1-germacyclopent-3-ene,[18] which was prepared in 69% yield by methylmagnesium bromide treatment of 1,1-dichloro-1-germacyclopent-3-ene, obtained in 58% yield from 1,3-butadiene and dichlorogermylene−dioxane complex.[19] After distillation **2** was isolated in 50% yield as a colorless liquid; bp 59 °C/20 Torr. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.27 s (3H, CH_3), 0.29 s (3H, CH_3), 0.99 d (2H, CH_2, $J = 15$ Hz), 1.38 d (2H, CH_2, $J = 15$ Hz), 3.49 s (1H, CH). ^{13}C NMR ($CDCl_3$, 300 MHz): δ −1.71 q (CH_3), −0.31 q (CH_3), 16.75 t (CH_2), 59.02 d (CH). IR (Ar matrix, 12 K): 3019.3 (w), 3004.2 (m), 2992.3 (m), 2956.6 (w), 2922.5 (w), 2806.0 (vw), 1413.6 (w), 1402.3 (w), 1385.0 (m), 1372.9 (vw), 1245.7 (w), 1240.3 (m), 1178.5 (m), 1170.1 (w), 1023.9 (vw), 970.4 (w), 926.1 (m), 919.6 (w), 832.9 (s), 823.6 (s), 811.6 (m), 808.9 (s), 806.1 (vs), 797.5 (w), 778.6 (vw), 712.9 (vw), 657.8 (w), 654.6 (w), 614.1 (m), 610.9 (m), 609.3 (m), 587.6 (m), 521.4 (m) cm^{-1}. EIMS: *m/z* (relative intensity) (given for ^{74}Ge) 159 (35, M − CH_3), 131 (40), 105 (45), 104 (45), 89 (100). Anal. Calcd for $C_6H_{12}GeO$: C, 41.72; H, 7.00; Ge, 42.02. Found: C, 41.78; H, 7.12; Ge, 42.19.

1,1,3,4-Tetramethyl-3-germa-6-oxabicyclo[3.1.0]hexane (3) was prepared in 50% yield (colorless liquid, bp 65 °C/16 Torr) by the epoxidation of 1,1,3,4-tetramethyl-1-germacyclopent-3-ene[20] similarly to the procedure briefly described above for **2**. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.16 s (3H, CH_3-Ge), 0.19 s (3H, CH_3Ge), 0.92 d (2H, CH_2, $J = 15$ Hz), 1.29 s (6H, CH_3), 1.34 d (2H, CH_2, $J = 15$ Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ −2.16 q (CH_3Ge), −0.93 q (CH_3Ge), 20.58 q (CH_3), 24.39 t (CH_2), 69.49 s (>C<). IR (Ar matrix, 12 K): 3009.7 (w), 2999.5 (w), 2968.8 (m), 2955.2 (vw), 2946.3 (w), 2937.5 (w), 2927.9 (w), 2916.3 (m), 2884.3 (vw), 2850.2 (vw), 2816.2 (vw), 1462.8 (m), 1438.6 (w), 1412.9 (w), 1404.8 (w), 1390.3 (vw), 1379.1 (m), 1374.3 (m), 1244.4 (vw), 1238.1 (m), 1219.7 (vs), 1171.8 (m), 1159.2 (m), 1125.1 (vw), 1060.8 (m), 1016.7 (m), 903.2 (w), 857.9 (vs), 832.0 (s), 829.8 (m), 808.8 (m), 796.9 (m), 690.1 (w), 686.0 (w), 682.7 (w), 675.7 (m), 608.8 (m), 586.8 (m), 579.0 (w) cm^{-1}. EIMS: *m/z* (relative intensity) (given for ^{70}Ge) 183 (100, M − CH_3), 165 (14), 157 (65), 141 (30), 115 (31), 101 (21), 100 (15), 85 (50). Anal. Calcd for $C_8H_{16}GeO$: C, 47.85; H, 8.03: Ge, 36.15. Found: C, 47.69; H, 7.89; Ge, 35.99.

Octamethylcyclotetragermoxane (4) was prepared in 89% yield by utilizing the Brown and Rochow method[21] and further purified by sublimation. ^1H NMR (CCl_4): 0.52 ppm. EIMS: *m/z* (relative intensity) (given for ^{70}Ge) 449 (62, M − CH_3), 333 (100), 317 (13), 217 (10), 115 (12). IR (Ar matrix, 12 K): 3008.3 (sh), 2996.0 (w), 2919.0 (vw), 2902.3 (vw), 2899.1 (vw), 2871.2 (vw), 1419.5 (vw), 1410.3 (vw), 1246.4 (m), 1238.2 (w), 863.1 (sh), 858.9 (m), 849.9 (s), 828.1 (m), 823.9 (m), 807.5 (vs), 803.5 (s), 755.1 (m), 629.3 (m), 602.9 (w), 594.6 (m), 588.7 (m), 534.4 (m), 521.7 (w) cm^{-1}.

Vacuum Pyrolysis−Matrix Isolation Spectroscopy. The vapors of **2** and **3**, kept at about −30 °C, or **4**, held at 60−70 °C, were passed through the tantalum foil resistively heated quartz pyrolyzer (8 mm internal diameter, 50 mm length), flanged to a vacuum chamber of the multisurface cryogenic apparatus.[22] The pressure and temperature in the pyrolysis zone were varied from 1 to 1×10^{-4} Torr and 500 to 950 °C, respectively. The pyrolysis products were cocondensed at 12−14 K with a large excess of argon (1:1000) on the reflective rhodium-plated copper surfaces, located at a distance of 20 mm from the pyrolyzer orifice. The multisurface substrate

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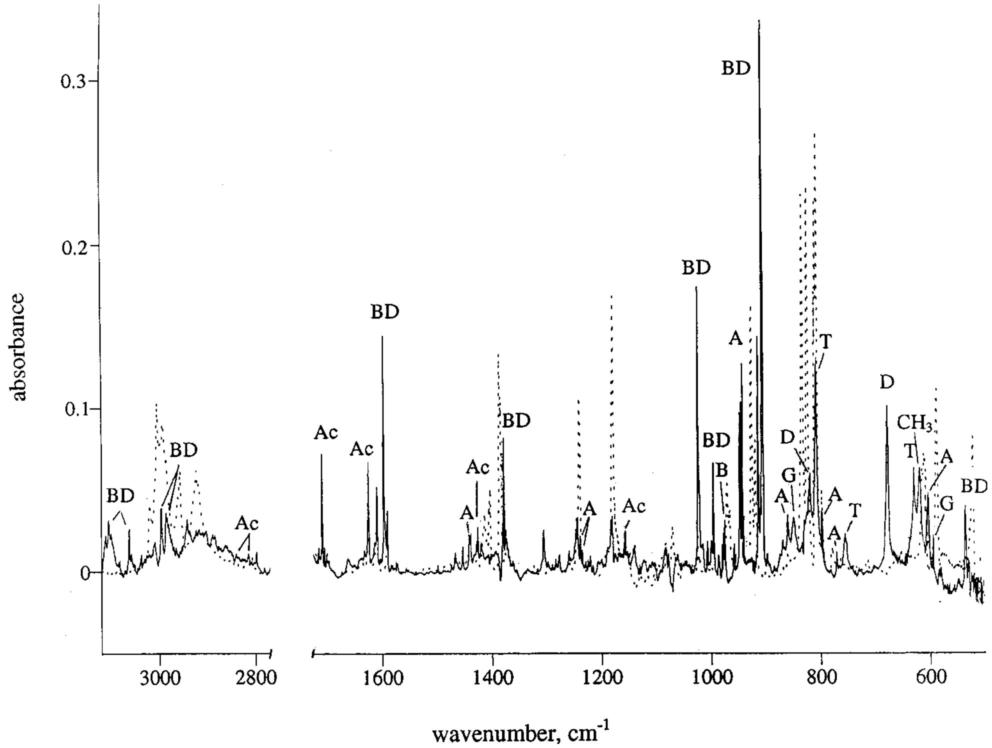

Figure 1. IR spectra (Ar, 12 K) of **2** (dashed line) and of the pyrolysis (10^{-4} Torr, 700 °C) products of **2** (solid line), shown after subtraction of the spectrum of **2**. Labeled peaks: (**A**) germanone **1**; (**B**) GeO; (**D**) cyclodigermoxane **6**; (**T**) cyclotrigermoxane **7**; (**Ac**) acrolein; (**BD**) butadiene; (**G**) germene **9**.

was cooled with the help of a closed-cycle Displex CSW-202 refrigerator from Air Products. The matrixes were analyzed with the IBM 98 FTIR spectrometer equipped with a liquid-nitrogen-cooled HgCdTe detector. The spectra were collected in the range of 500−4000 cm^{-1} with 0.5 cm^{-1} resolution using the reflection of the infrared beam from the cold substrate surfaces.

The controlled warm-up experiments of deposited matrixes to diffusion temperatures of 35−45 K, imperative for identification of spectral absorptions of transient species, were carried out with the help of a built-in heater. The matrixes from the pyrolysates of **2** and **3** were also warmed to room temperature under vacuum for collecting the final pyrolysis products into a liquid-nitrogen-cooled trap. The collected condensates were further examined by GC-MS and by taking their FTIR spectra after redeposition into argon matrixes at 12 K.

Calculations. The ground-state optimized geometries for germanone **1**, parent germanone $H_2Ge{=}O$ (**5**), and the cyclodimer of **1**—1,1,3,3-tetramethyl-1,3-cyclodigermoxane (**6**)—as well as their harmonic vibrational frequencies and infrared intensities were computed at the density functional theory B3LYP level of theory[23] with the 6-311G(d,p) basis set of triple-ζ quality.[24] The calculations were performed with the Gaussian 94 program package[25] running on an NEC SX-3 supercomputer. The vibrational analysis of computed frequencies was carried out with the assistance of the Xmol vibration visualization package[26] installed on an SGI computer and also on the basis of potential energy distributions (PED) for normal vibrational modes calculated with the help of the REDONG program.[27] The force constants in internal coordinates for the germanones **1** and **5** were calculated from the B3LYP/6-311G-(d,p) second derivatives by REDONG approximation.

Results and Discussion

FTIR Spectra of Matrix-Isolated Pyrolysis Products from Epoxide 2. The IR spectrum of argon matrix isolated precursor **2** and that of the pyrolysis products of **2**, produced at a temperature of 700 °C and a pressure of ~10^{-4} Torr in the pyrolysis zone, are shown in Figure 1. In the solid-line spectrum of pyrolysis products, shown after subtraction of the dotted-line spectrum of **2**, we observed the prominent peaks of *trans*- and *s-cis*-1,3-butadiene (BD)[28] and several of the most intense bands (labeled by **T**) of the cyclotrimer of germanone **1**, hexamethylcyclotrigermoxane (**7**), identified by comparison with the literature IR data[29] and detected peaks

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for matrix-isolated **7**. These products as well as the tetramer of **1**, cyclotetragermoxane **4**, were recently identified as the only final products of the thermal decomposition of **2** under flow conditions;[14] therefore, their observation in our IR spectra was expected. Besides the bands of these products, a set of new bands, denoted by **A**, **B**, **D**, **G**, and **Ac** labels in Figure 1, as well as the absorption of the CH_3 radical at 618.4 cm^{-1} have been detected. After the matrix was warmed to room temperature, the pyrolysate was collected in a liquid-nitrogen-cooled trap and then the condensate was redeposited with an excess of argon into a cryogenic matrix at 12 K for FTIR spectroscopic examination and also analyzed by GC-MS. In the IR spectrum of the redeposited matrix the bands labeled by **A**, **B**, **D**, and **G** were absent, while those of 1,3-butadiene and absorptions denoted by **Ac** have been retained. The GC-MS analysis revealed, besides the 1,3-butadiene, the presence of one more non-germanium-containing product, which by comparison with the mass spectrum of authentic sample was identified as acrolein. As a result, the **Ac**-labeled IR peaks have been attributed to matrix-isolated acrolein, in agreement with the literature spectral data.[30]

Annealing of the matrix, whose spectrum is shown in Figure 1 by a solid line, from 12 to 40 K resulted in the disappearance of the **A**, **B**, and **G** peaks, weakening of **D**-labeled absorptions and growth of the **T**-labeled bands of the cyclotrimer **7**. An increase in pressure in the pyrolysis zone from 10^{-4} to 10^{-1} Torr resulted in the similar depletion of the **A**, **B**, and **G** peaks and growth of the absorptions of **7**; however, the **D**-labeled bands have been observed to grow in these experiments instead of weakening as well. This suggests that the **D** peaks belong to a more kinetically stable transient species than the three whose absorptions are labeled by **A**, **B**, and **G**, respectively.

The **B** band, located in the 973−981 cm^{-1} spectral region and clearly exhibiting the germanium natural isotopic splitting, is assigned to germanium monoxide, GeO, in accord with the literature matrix isolation IR data.[8,9] The **A**-labeled set of bands we attribute to dimethylgermanone **1**, which is expected to be generated along with 1,3-butadiene in the $4 \rightarrow [2 + 2]$ unimolecular thermal cycloreversion of germaoxetane (**8**) by analogy with the earlier studied vacuum pyrolysis of the silicon analogue of **2**.[16] The compound **8** was suggested to be formed as an intermediate in the pyrolysis of epoxide **2**,[14] as shown in Scheme 1. The assignment of the **A** bands to **1** is based on their behavior in the matrix warm-up experiments and under the conditions of increased pressure in the reaction zone, boosting the number of intermolecular collisions in the gas phase, and on the observation of the same set of peaks in the IR spectra of matrix-isolated pyrolysis products of another precursor, epoxide **3**. The proposed assignment is in excellent agreement with the B3LYP/6-311G(d,p) calculated IR spectrum of **1** (Table 1), which provides valuable guidance for identification of germanone **1**.

The possibility of attributing the **A** bands to methyl(methoxy)germylene, CH_3GeOCH_3, has also been considered but is unlikely for several reasons. Our DFT-B3LYP/6-311G(d,p) calculations predict that a more stable *trans*-germylene should not exhibit any IR bands in the 750−1050 cm^{-1} region,[31] while we observed two intense peaks (Figure 1 and Table 1) in this spectral range. In spite of the calculated higher thermodynamic stability of germylene relative to germanone **1** (by 5−12 kcal/mol, according to Schleyer et al.,[5] and by 7.2 kcal/mol from our B3LYP/6-311G(d,p) calculations), the latter is separated from the former by a B3LYP/6-311G-

Scheme 1

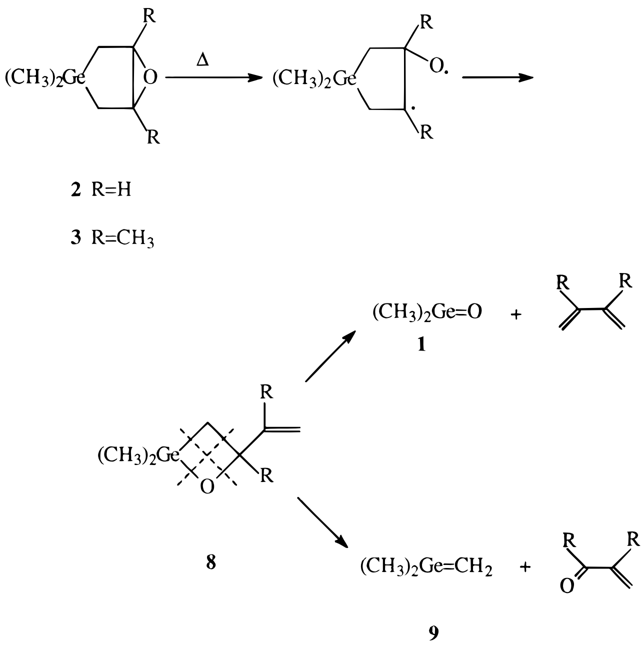

Table 1. Vibrations of Dimethylgermanone, $(CH_3)_2Ge{=}O$ (1)

mode	sym	freq (cm^{-1}) calcd[a]	freq (cm^{-1}) obsd	PED (%) and assignt
1	a_2	48(0)[b]		100 CH_3 torsion, op
2	b_1	69(0)		100 CH_3 torsion, ip
3	a_1	172(0.2)		100 CGeC scissor
4	b_1	182(7)		100 GeC_2 wag
5	b_2	226(34)		100 GeC_2 in-plane rock
6	a_1	546(4)		100 Ge−C sym str
7	b_2	584(37)	605.0 s[c]	100 Ge−C asym str
8	a_2	724(0)		96 CH_3 sym rock
9	b_2	768(33)	770.7 m	88 CH_3 asym in-plane rock
10	b_1	788(16)	794.8 m	94 CH_3 rock
11	a_1	860(26)	857.4 m	85 CH_3 sym in-plane rock
12	a_1	954(76)	943.0 vs[c]	100 Ge=O str
13	b_2	1264(5)	1234.0 w	100 CH_3 asym deform rock
14	a_1	1270(9)	1239.1 w	100 CH_3 sym deform rock
15	b_2	1449(2)		97 CH_3 deform
16	a_2	1456(0)		89 CH_3 deform
17	a_1	1457(6)		96 CH_3 deform
18	b_1	1469(17)	1441.2 w	88 CH_3 deform
19	b_2	3035(2)		100 CH_3 str
20	a_1	3038(4)		100 CH_3 str
21	b_1	3108(0)		100 CH_3 str
22	b_1	3110(11)		100 CH_3 str
23	b_2	3147(2)		100 CH_3 str
24	a_1	3148(2)		100 CH_3 str

[a] B3LYP/6-311G(d,p). [b] Intensity, km/mol. [c] ^{74}Ge isotopomer.

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[30] (a) Blom, C. E.; Müller, R. P.; Günthard, Hs. H. *Chem. Phys. Lett.* **1980**, *73*, 483. (b) Harris, R. K. *Spectrochim. Acta* **1964**, *20*, 1129.

[31] B3LYP/6-311G(d, p) calculated vibrational frequencies (ν, cm^{-1}) and infrared intensities (I, km/mol) for *trans*-germylene CH_3OGeCH_3: ν (I), 46 (0.3), 129 (0.03), 167 (0.6), 171 (6), 294 (5), 530 (49), 584 (67), 650 (0.04), 745 (27), 1073 (200), 1172 (0.68), 1192 (7), 1235 (14), 1448 (7), 1449 (14), 1477 (18), 1488 (1), 1502 (7), 2979 (89), 3007 (9), 3046 (48), 3063 (41), 3072 (17), 3122 (8).

Table 2. Vibrations of 1,1,3,3-Tetramethyl-1,3-digerma-2,4-dioxetane (6)

		freq[a]					freq[a]		
mode	sym	calcd[b]	obsd	assignt	mode	sym	calcd[b]	obsd	assignt
1	a_u	59(0)		CH_3 sym torsion	28	b_{1u}	842(87)		CH_3 rock
2	b_{2u}	63(0)		GeC_2 sym rock	29	b_{3u}	849(111)	819.2 m	CH_3 sym rock op
3	b_{3g}	69(0)		CH_3 torsion op	30	a_g	861(0)		sym CH_3 sym rock
4	b_{2g}	76(0)		CH_3 torsion	31	b_{1g}	1274(0)		CH_3 asym deform rock ip
5	b_{1u}	83(0)		CH_3 torsion ip	32	b_{2u}	1278(30)		CH_3 asym deform rock op
6	a_u	97(0)		GeC_2 twist op	33	b_{3u}	1279(19)		CH_3 sym deform rock ip
7	b_{1u}	153(0)		GeC_2 wag ip	34	a_g	1282(0)		CH_3 sym deform rock op
8	a_g	155(0)		GeC_2 sym scissor	35	a_u	1454(0)		CH_3 deformation
9	b_{1g}	158(0)		GeC_2 rock ip	36	b_{1g}	1455(0)		CH_3 deformation
10	b_{2g}	159(0)		GeC_2 wag op	37	b_{3g}	1457(0)		CH_3 deformation
11	b_{3u}	167(5)		GeC_2 asym scissor	38	b_{2u}	1458(5)		CH_3 deformation
12	b_{3g}	203(0)		GeC_2 twist ip	39	b_{3u}	1462(6)		CH_3 deformation
13	a_g	315(0)		OGeO sym in-plane ring stretch	40	a_g	1465(0)		CH_3 deformation
14	b_{2u}	316(60)		OGeO sym out-of-plane “butterfly” bend	41	b_{2g}	1465(0)		CH_3 deformation
15	b_{2g}	558(0)		GeOGe in-plane rock	42	b_{1u}	1469(20)		CH_3 deformation
16	b_{3u}	559(6)		asym Ge−C sym str	43	b_{1g}	3039(0)		CH str
17	a_g	577(0)		sym Ge−C sym str	44	b_{2u}	3039(12)		CH str
18	b_{1g}	600(0)		Ge−C asym str op	45	b_{3u}	3041(11)		CH str
19	b_{2u}	606(65)		Ge−C asym str ip	46	a_g	3041(0)		CH str
20	b_{1u}	615(75)		GeOGe asym in-plane ring stretch	47	a_u	3116(0)		CH str
21	b_{3u}	665(448)	676.5 s	OGeO asym in-plane ring stretch	48	b_{3g}	3117(0)		CH str
22	a_g	701(0)		GeOGe sym in-plane ring stretch	49	b_{2g}	3118(0)		CH str
23	b_{1g}	761(0)		CH_3 sym rock ip	50	b_{1u}	3118(31)		CH str
24	b_{3g}	762(0)		CH_3 rock	51	b_{1g}	3134(0)		CH str
25	a_u	765(0)		CH_3 rock	52	b_{3u}	3134(21)		CH str
26	b_{2u}	773(73)		CH_3 asym rock ip	53	b_{2u}	3135(8)		CH str
27	b_{2g}	814(0)		CH_3 rock	54	a_g	3135(0)		CH str

[a] cm^{-1}. [b] B3LYP/6-311G(d,p). [c] Intensity, km/mol.

(d,p) barrier of 62 kcal/mol, calculated in the present work. We believe that such a high barrier precludes a ground-state thermal isomerization of **1** into germylene in the gas phase at the pyrolysis temperatures of precursor **2** (700−800 °C).

We assigned the **G**-labeled bands to 1,1-dimethyl-1-germene, $(CH_3)_2Ge{=}CH_2$ (**9**), after comparison with the recently detected IR spectrum of matrix-isolated **9**,[32] in which the peaks at 595.4 and 847.1 cm^{-1}, also observed in the present work, have shown the highest intensities. We suggest that the germene **9** is formed as a product of the parallel 4 → 2 + 2 cycloreversion route for the germaoxetane **8**, proceeding via breaking of the Ge−O bond in the ring and subsequent elimination of acrolein (Scheme 1).

As to **D**-labeled absorptions, observed at 676.5 and 819.2 cm^{-1}, they are tentatively assigned to the cyclodimer of **1**, 1,1,3,3-tetramethyl-1,3-cyclodigermoxane (**6**), on the basis of their slower depletion in comparison to the bands attributed to transient species **1**, **9**, and GeO during matrix annealing and their observation in the spectra of the pyrolysis products produced under increased pressure in the reaction zone. This assignment is in reasonable agreement with the calculation of vibrational frequencies and IR intensities for 1,3-cyclodigermoxane **6** (Table 2), predicting that the computed bands at 665 and 849 cm^{-1} of the antisymmetric OGeO in-plane stretching and CH_3 symmetric rocking modes, respectively, should be the most intense in the IR spectra. The observation of the same two bands (at 676.5 and 819.2 cm^{-1}) in the IR spectra of pyrolysis products of the other precursors for **1**, such as epoxide **3** and cyclotetragermoxane **4**, provides additional support for the suggested formation of 1,3-cyclodigermoxane **6** and its cryotrapping in argon matrixes.

FTIR Spectra of Matrix-Isolated Pyrolysis Products from Epoxide 3. In Figure 2b is shown the spectrum of matrix-isolated pyrolysis products from **3**, produced at a temperature of 700 °C and a pressure of $\sim 10^{-4}$ Torr in the reaction zone. The peaks of *s-cis-* and *trans*-2,3-dimethyl-1,3-butadiene (**DB**)[33] were found to be the most intense. Besides that, the prominent peaks of the cyclogermoxane **7**, denoted by **T**, and those labeled by **A**, **B**, **D**, and **G**, already observed in the IR spectra of matrix-isolated pyrolysis products of epoxide **2**, have all been detected in this spectrum as well. In addition, several new bands, denoted by **I**, have been observed.

After the increase of pyrolysis temperature to 800 °C, we observed a further enhancement of the peaks of 2,3-dimethylbutadiene (**DB**) and the **I**-labeled bands along with an increase of the **B**-labeled band of GeO and that of the CH_3 radical at the expense of the **A**-labeled bands, attributed to germanone **1**, in the spectrum given in Figure 2c. Matrix isolation studies on the Si analogue of **1** dimethylsilanone, $(CH_3)_2Si{=}O$, have shown that the latter thermally dissociates at elevated temperatures into silicon oxide and CH_3 radical.[16] Therefore, we suggest that the observed changes in the spectrum of

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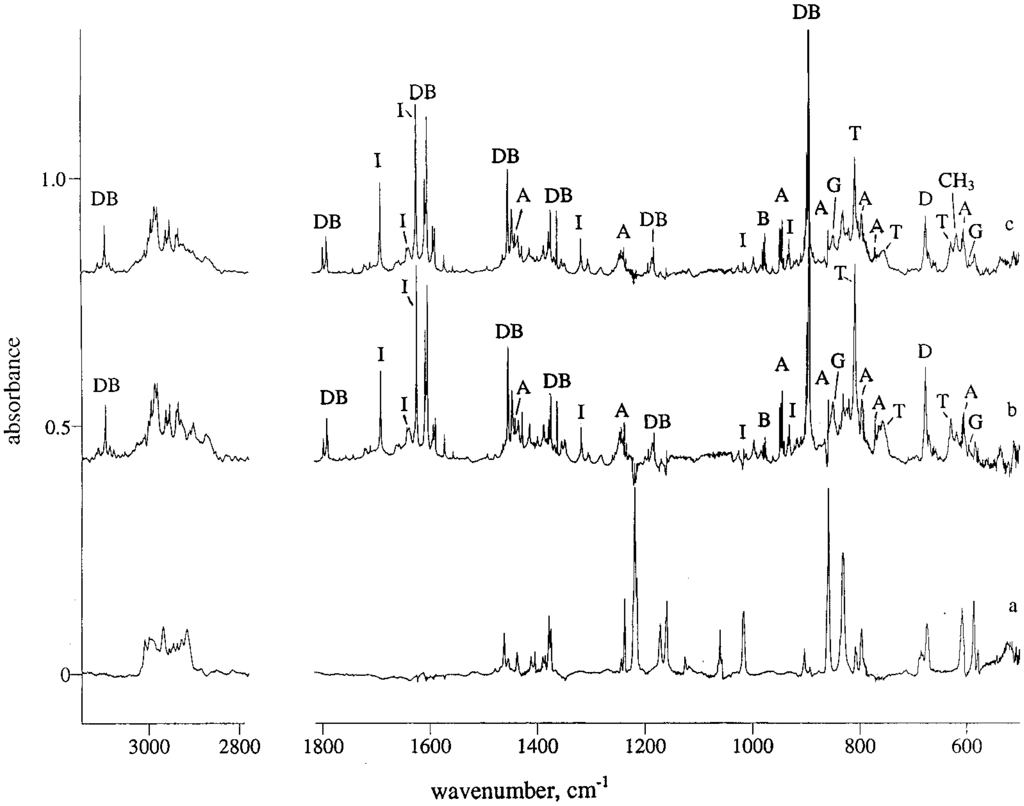

Figure 2. IR spectra (Ar, 12 K) of epoxide **3** (a) and pyrolysis (10^{-4} Torr) products of **3** at (b) 700 °C and (c) 800 °C. The spectrum of **3** is subtracted from the spectra shown under (b) and (c). Labeled peaks: (**A**) germanone **1**; (**B**) GeO; (**D**) cyclodigermoxane **6**; (**T**) cyclotrigermoxane **7**; (**I**) isopropenyl methyl ketone; (**DB**) 2,3-dimethylbutadiene; (**G**) germene **9**.

the pyrolysate from **3** under high temperatures can be similarly explained by the decomposition of **1** into germanium oxide and CH_3 radical, as shown by the equation:

$$(CH_3)_2Ge{=}O \rightarrow GeO + 2CH_3^{\bullet}$$

An increase of the pyrolysis temperature above 800 °C resulted in the appearance of a strong ethylene absorption, peaking at 947.5 cm^{-1}, which overlapped the multiplet of germanone **1** in the 943−948 cm^{-1} spectral region. Since in the earlier matrix isolation studies[13] the germanone **1** was generated at a temperature higher than that utilized in the present work, this IR feature of **1** could not be clearly distinguished from broadened ethylene absorption and therefore was not reported in the preliminary publication.[13a]

Annealing of the matrix, whose IR spectrum is shown by a dashed line in Figure 3 with the bands of precursor **3** not subtracted, caused the depletion of the **A**-, **B**-, **D**-, and **I**-labeled peaks and growth of the **T**-labeled peaks of cyclotrigermoxane **7**, as indicated by the full line spectrum. The **I**-labeled peaks and those of butadiene **DB** were observed in the IR spectrum produced after the matrix, whose spectrum is shown by a solid line in Figure 3, was warmed to room temperature; the reaction products were collected into a liquid-nitrogen-cooled trap and then redeposited in an argon matrix at 12 K. The **A**-, **B**-, and **D**-labeled peaks were all absent in this spectrum. The GC-MS analysis of the collected condensate allowed us to identify isopropenyl methyl ketone by comparison with the mass spectrum of an authentic sample. On the basis of literature IR data for this compound[34a,b] and for the $CH_2{=}C(CH_3)$ group frequencies in methacrolein[34c] we assigned the peaks, denoted by **I** in Figures 2 and 3, to isopropenyl methyl ketone.

The peaks denoted by **G** in Figures 1 and 2 were overlapped in the spectra, shown in Figure 3, by the intense absorptions of epoxide **3**. They could be distinguished only after subtraction of the bands of **3** from the dashed-line spectrum in Figure 3, producing the spectrum shown in Figure 2b. The **G**-labeled peaks were clearly observed at 595.4 and 804.1 cm^{-1} and as a triplet in the 847−850 cm^{-1} region of the expanded 590−980 cm^{-1} section of this spectrum, as shown in Figure 4. These bands match the three most intense IR absorptions of germene **9**.[32] The triplet maxima, found at 849.4, 848.3, and 847.1 cm^{-1}, are in agreement with the previously observed[32a] $^{70}Ge/^{72}Ge/^{74}Ge$ natural isotopic splitting of the band of the Ge=C stretching mode coupled with the CH_3 rock in **9** (Table 3). These observations make the assignment of the **G** bands to the germene **9** most likely. The generation of **9** from the epoxide **3** probably proceeds via extrusion of isopropenyl methyl ketone from the intermediate germaoxetane derivative **10**, as shown in Scheme 1. The 1,3-cyclodimer of the germene **9** is probably also formed. This is indicated by the **C**-marked band observed as a shoulder on the **A**-labeled band at 602.4 cm^{-1} (Figure 4), matching the most intense absorption in the IR spectrum of the matrix-isolated 1,3-cyclodimer of **1**.[32a]

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[34] (a) Bienvenue, A.; Duchatellier, B. *Tetrahedron* **1972**, *28*, 833. (b) Cottee, F. H.; Straughan, B. P.; Timmons, C. J.; Forbes, W. F.; Shilton, R. *J. Chem. Soc. B* **1967**, 1146. (c) Durig, J. R.; Qiu, J.; Dehoff, B.; Little, T. S. *Spectrochim. Acta* **1986**, *42A*, 89.

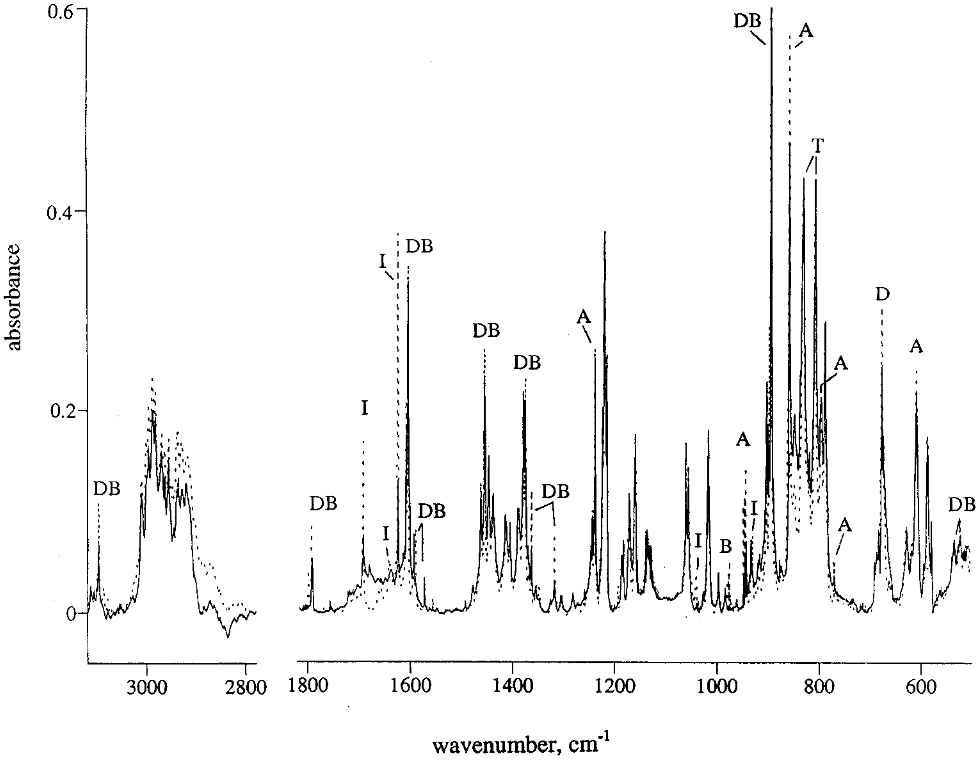

Figure 3. IR spectra of pyrolysis (10^{-4} Torr, 700 °C) products of **3** (Ar, 12 K) (dashed line) and of the same matrix after annealing from 12 to 40 K (solid line). Labeled peaks: (**A**) germanone **1**; (**B**) GeO; (**D**) cyclodigermoxane **6**; (**T**) cyclotrigermoxane **7**; (**I**) isopropenyl methyl ketone; (**DB**) 2,3-dimethylbutadiene.

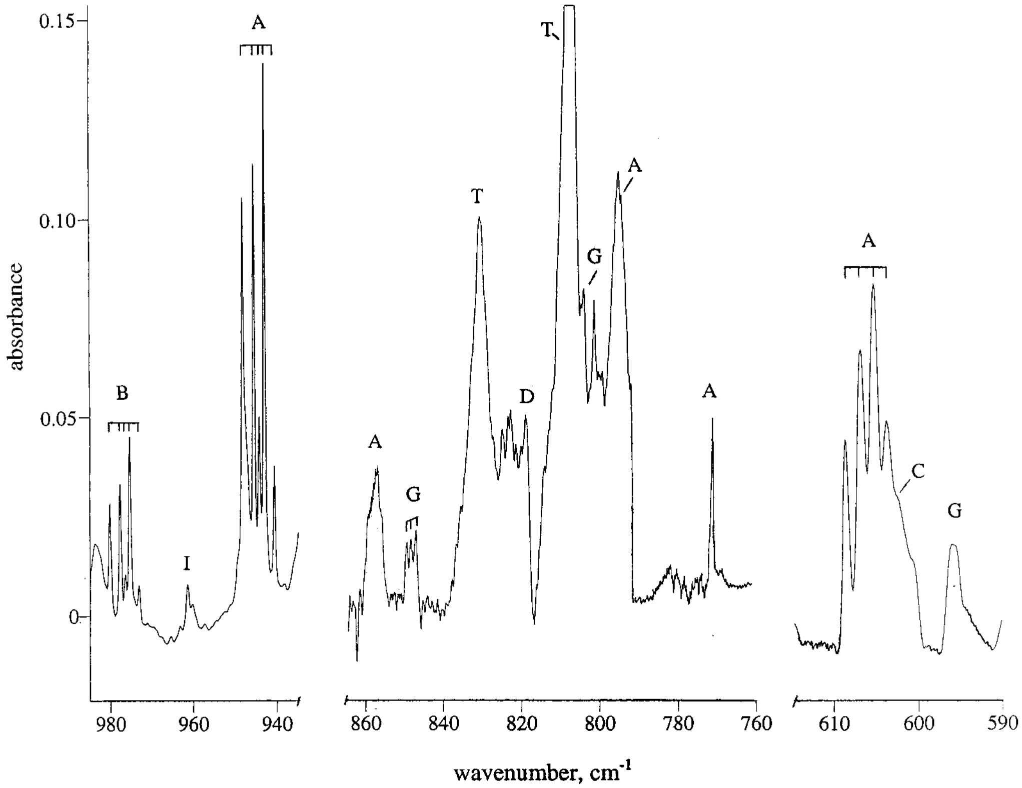

Figure 4. The expanded 980–940, 860–760 and 610–590 cm^{-1} sections of the IR spectrum of the pyrolysis products of **3** shown in Figure 2b. Labeled peaks: (**A**) germanone **1**; (**B**) GeO; (**D**) cyclodigermoxane **6**; (**T**) cyclotrigermoxane **7**; (**I**) isopropenyl methyl ketone; (**G**) germene **9**; (**C**) dimer of germene.

The assignments of the **A** bands to germanone **1** and of the **B**-labeled absorption to monomeric GeO are further supported in these experiments by observation of the germanium isotopic structure of the IR bands in the 602–609, 940–949 and 970–981 cm^{-1} spectral regions (Figure 4), which are found to be in good agree-

Table 3. Infrared Absorptions (cm^{-1}) of Germanium Isotopomers of Dimethylgermanone (1) and Dimethylgermene (9) in a Solid Argon Matrix

	vibrational mode		freq			Δν	
			calcd[a]	obsd		calcd	obsd
$(CH_3)_2Ge{=}O$ (**1**)	Ge=O str	^{70}Ge	959.1	948.2	70/72	2.7	2.7
		^{72}Ge	956.4	945.5			
		^{73}Ge	955.1	944.2	72/74	2.6	2.5
		^{74}Ge	953.8	943.0			
		^{76}Ge	951.4	940.6	74/76	2.4	2.4
	Ge−C asym str	^{70}Ge	587.7	608.5	70/72	1.8	1.8
		^{72}Ge	585.9	606.7			
		^{73}Ge	585.0		72/74	1.7	1.7
		^{74}Ge	584.2	605.0			
		^{76}Ge	582.6	603.5	74/76	1.6	1.5
	Ge−C sym str	^{70}Ge	547.2				
		^{72}Ge	546.7				
		^{73}Ge	546.4				
		^{74}Ge	546.2				
		^{76}Ge	545.7				
$(CH_3)_2Ge{=}CH_2$ (**6**)	Ge=C str, CH_3 rock	^{70}Ge	849.4[b]	849.6[c]			
		^{72}Ge	848.3[b]	848.4[c]			
		^{74}Ge	847.1[b]	847.3[c]			

[a] B3LYP/6-311G(d, p). [b] Present work. [c] Previous observation.[32a]

ment with the literature data on GeO[8,9] and our calculations for the germanium isotopomers of **1** (Table 3).

The **D** bands, attributed to cyclodigermoxane **6**, were observed in the same region as in the spectra of pyrolysis products from **2**. They were also present in the spectra of the pyrolysate produced from **3** under increased pressure in the reaction zone, i.e., under conditions for which the other transient molecules, **1**, **9** and GeO, did not survive.

Mechanistic Aspects of Vacuum Pyrolysis of Epoxides 2 and 3. The matrix isolation−vacuum pyrolysis studies of these precursors have demonstrated that they very likely decompose along two parallel pathways and yield not only the germanone **1** but also the transient germene **9**, as shown in Scheme 1. The thermal decomposition route, leading to the germene, has not been considered earlier for the epoxides **2** and **3** and their derived analogues. However, the germanone and germene were suggested to be formed via two 4 → 2 + 2 parallel decomposition processes of the four-membered germaoxetanes[1a] which have been accessed through the nearly quantitative 2 + 2 cycloadditions of germenes to ketones and aldehydes.[35] The germaoxetane was even proposed to be a convenient storage for the transient germene after observation of only "the germene" channel for the easy cycloreversion of the four-membered ring compound obtained by cycloaddition of $Me_2Ge{=}C(SiMe_3)_2$ to benzophenone.[36] We believe that these literature data on germaoxetanes, which have also been considered as intermediates in the thermolysis of epoxide **2**,[14] and a sure identification of the 1,3-butadiene 2,3-dimethylbuta-1,3-diene and acrolein and isopropenyl methyl ketone in our experiments provide a solid foundation for the suggested mechanism (Scheme 1) of vacuum pyrolyses of **2** and **3**.

Vacuum Pyrolysis−Matrix Isolation FTIR Study of Germoxane 4. These experiments were carried out with the idea of producing germanone **1** in a single-channel monomolecular decomposition of a precursor, as was expected for octamethyltetragermoxane **4**[15] in accordance with the scheme

$$[(CH_3)_2GeO]_4 \rightarrow [(CH_3)_2GeO]_3 + (CH_3)_2Ge{=}O$$

In Figure 5b is shown the IR spectrum of matrix-isolated pyrolysis products from **4**, produced at a temperature of 700 °C in the reaction zone. The **D**-labeled peaks of the cyclodimer **6** and the **T**-labeled absorptions of the cyclotrimer **7** were observed along with the strong bands of undecomposed **4**, whose spectrum is given in Figure 5a. Very weak, but clear, IR absorptions of the isotopomers of germanone **1** were observed in the expanded 940−980 cm^{-1} region (inset in Figure 5) of the spectrum of pyrolysis products from **4**. The attempts to increase the yield of **1** by elevating the temperature in the pyrolysis zone were unsuccessful, as in the studies of epoxides **2** and **3**. They resulted in the growth of the **B**-labeled absorption of the isotopomers of GeO as well as appearance of the peaks of ethylene and CH_3 radical, instead of desirable enhancement of germanone features in the spectra. The very low yield of **1** in these experiments can be explained by a higher thermal stability of germoxane **4** with respect to epoxides **2** and **3**, which implied the use of higher temperatures for destructive pyrolysis of the germanone. One more explanation can be deduced from the observation of a prominent IR absorption assigned to germanone cyclodimer **6** (Figure 5b), which leads to the assumption that under the vacuum pyrolysis conditions used a parallel monomolecular decomposition channel for **4** exists, as shown by the scheme

$$[(CH_3)_2GeO]_4 \rightarrow [(CH_3)_2GeO]_2 + [(CH_3)_2GeO]_2$$

The possibility of the suggested route is based on the known ability of the four-membered rings with the Ge−O endocyclic bond to dimerize readily at ambient temperatures into eight-membered rings and dissociate back to the initially smaller rings after heating.[1] It is likely that this route mainly contributes to production of cyclodimer **7**, which is probably also formed by a

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(36) Wiberg, N.; Kim, C. K. *Chem. Ber.* **1990**, *90*, 2996, 2980.

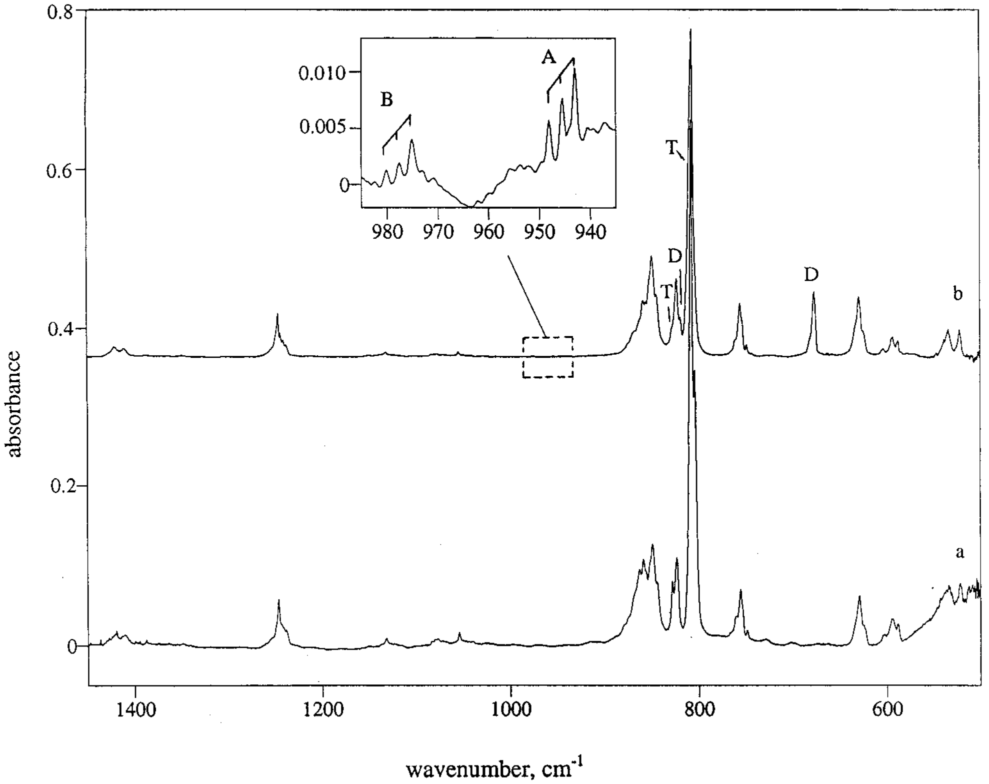

Figure 5. IR spectra (Ar, 12 K): (a) **4**; (b) pyrolysis (10^{-4} Torr, 700 °C) products of **4**. Labeled peaks: (**A**) germanone **1**; (**B**) GeO; (**D**) cyclodigermoxane **6**; (**T**) cyclotrigermoxane **7**. All unlabeled peaks belong to **4**.

partial dimerization of germanone **1** proceeding, as in the case of silanones,[16] with no barrier. This suggestion agrees with our vacuum pyrolysis–MS studies of **4**, which involved the energetic measurements on characteristic ions of **1**, **4**, **6**, and **7**. They have shown that in the gas-phase beam of pyrolysis products of **4** the cyclodimer **6** was present as a major component along with a smaller amount of the cyclotrimer **7** and a very low flow concentration of germanone **1**.

Germanone 1. Molecular Geometry. Our B3LYP/6-311G(d,p) calculations yielded a planar (C_{2v}) optimized geometry for the singlet ground state of **1**, shown in Figure 6 along with the structure of the parent germanone **5** optimized at the same level of theory. The Ge=O bond lengths in both germanones are found to be almost identical (1.650 Å in **1** and 1.645 Å in **5**) and are somewhat shorter than those calculated by Schleyer et al.[5] with the DZ+P basis set by B3LYP and MP2 methods (1.657–1.675 Å) and slightly longer than the earlier SCF DZ+D computed value (1.63 Å) in **5**.[4a] The valence angles at the germanium, CGeC in **1** and HGeH in **5**, are calculated to be very close to each other (113.4 and 112.9°, respectively) and to the SCF calculated value of 112° for the parent germanone[4a] and agree with those computed in other work (111–117°).[5] The calculated Mulliken charge distributions and dipole moments indicate strong polarity of the Ge=O bonds in both germanones (Figure 6).

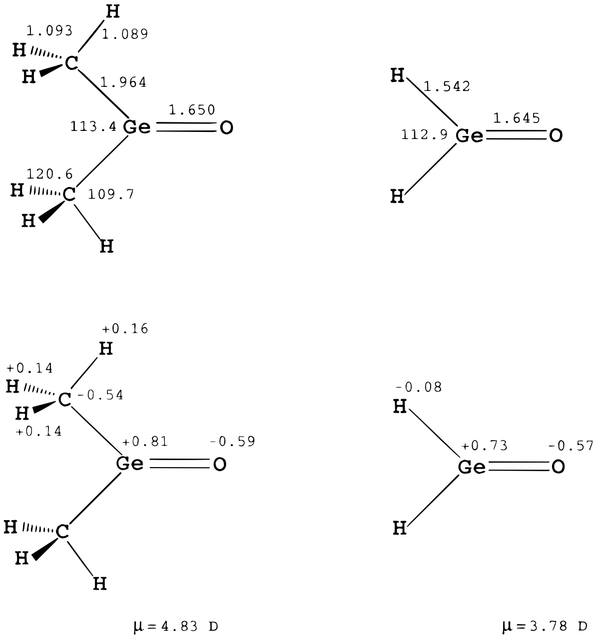

Figure 6. Optimized geometries, charge distributions, and dipole moments for germanones **1** and **5**.

IR Spectrum. A full assignment of the IR bands attributed to germanone **1** in our experiments has been suggested by comparison with the IR spectra of methylgermanes[37] and dimethylgermathione, $(CH_3)_2Ge=S$,[38] and inorganic germanones $F_2Ge=O$[6] and $H_2Ge=O$ (**5**),[7] and with the density functional theory (DFT)[23,39] calculated vibrational spectra of **5** and **1**, including the potential energy distributions (PED) for each vibrational

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(39) Wong, N. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

Table 4. Vibrations of Germanone $H_2Ge{=}O$ (5)

		freq (cm^{-1})			
			calcd		
mode	sym	obsd[a]	ref 4a[c]	present work[d]	PED (%) and assignt[f]
1	b_1		981	590(21)[e]	100 GeH_2 wag
2	b_2		627	594(52)	100 GeH_2 in-plane rock
3	a_1	(803.8)[b]	893	890(71)	100 GeH_2 scissor
4	a_1	961.9 964.3 966.6	1038	961(29)	100 Ge=O str
5	a_1	2076.6	2257	2112(35)	100 GeH_2 sym str
6	b_2	2079.6	2207	2117(171)	100 GeH_2 asym str

[a] Reference 7. [b] Tentative assignment.[7] [c] SCF DZ+D. [d] B3LYP/6-311G(d,p). [e] Intensity, km/mol. [f] Present work.

mode and IR absorptions for all germanium isotopomers of **1**. In our recent works we have shown the high reliability of the B3LYP/6-311G(d,p) approximation in predicting the spectra of transient silenes[40] and germenes.[32a,41] In the present work the same DFT method was tested as a tool for vibrational analysis of the spectra of germanones.

In Table 4 the observed frequencies for the parent $H_2Ge{=}O$ molecule[7] are compared with previously calculated SCF DZ+D frequencies[4a] and with the DFT spectral data computed in the present work. The latter values are found to be in excellent agreement with the experimental ones; therefore, the scaling procedure, usually applied to the SCF calculated frequencies, is unnecessary. Accordingly, we used the DFT computed frequencies for the dimethyl-substituted germanone **1** without further scaling.

The germanone **1** molecule has 24 normal vibrational modes; three of them are forbidden in the IR spectrum. Four infrared-active vibrations, predicted to be located below 500 cm^{-1}, could not be observed in our experiments. We have experimentally found 8 of the 17 expected fundamentals in the 500−4000 cm^{-1} spectral region.

The bands of the CH stretching vibrations of the methyl groups, located at 2850−3000 cm^{-1} in the spectra of methylgermanes,[37] were not observed due to their predicted low infrared intensity in **1** and also their overlapping with the bands of 1,3-butadiene or its dimethyl analogue and those of the other byproducts.

The suggested assignment of the observed band at 1441.2 cm^{-1} to the CH_3 deformation of b_1 symmetry is based on the location of this mode in the 1390−1460 cm^{-1} region, typical for this type of deformation in methylgermanes,[37] and on calculations predicting the b_1 vibration to be the strongest among the other CH_3 deformation modes in **1**.

The two observed weak bands at 1239.1 and 1234.0 cm^{-1} were attributed to the symmetric and antisymmetric CH_3 deformation rocking modes, respectively, in agreement with the calculation and with the known location of these modes in the 1200−1250 cm^{-1} region in the IR spectra of dimethyl-substituted germanes.[37]

For the assignment of the bands lying below 1000 cm^{-1}, where the stretching vibrations in **1** involving the atoms heavier than hydrogen are located, the observation of the isotopic splittings of some bands are in accord with the natural abundance of germanium and their comparison with the calculated frequencies for germanium isotopomers of **1** (Table 3) provided valuable assistance. The calculations predict that three modes, ν_6, ν_7, and ν_{12}, are sensitive to the variation of the isotopic mass of the germanium atom, indicating that they represent the stretching motions of the Ge−C and Ge=O bonds. The location of the Ge=O stretch is of particular interest. In the parent germanone **5** our calculations predict this mode to be found at 961 cm^{-1} (Table 4), which is in excellent agreement with the observation of an isotopically split band in the 961−967 cm^{-1} region of the spectrum of matrix-isolated **5**.[7] On the basis of the observed increase in the frequency of the Si=O streching mode on going from parent silanone $H_2Si{=}O$ (1202 cm^{-1})[42] to dimethylsilanone, $(CH_3)_2Si{=}O$ (1210 cm^{-1}),[16] one would expect the frequency of the Ge=O stretching vibration in the dimethyl-substituted germanone **1** to be also higher than in the parent molecule **5**. Nevertheless, our calculations predict the location of the Ge=O frequency in **1** at 954 cm^{-1} (Table 1), i.e., at lower energy than in **5** (Table 4). A possible explanation of these results comes from vibration visualization indicating that the Ge=O stretching modes in germanones **1** and **5** are virtually pure, while the Si=O stretch in $H_2Si{=}O$ is coupled with the SiH_2 scissor and therefore is red-shifted relative to that in dimethylsilanone.

The predicted location of the Ge=O stretch in **1** is in accord with the observation of the intense band in the 940−949 cm^{-1} region in our spectra attributed to **1**. The observed high intensity of this band is consistent with the calculated oscillator strength of the Ge=O stretch in **1** (79 km/mol), predicting this mode to be the most prominent peak in the infrared spectrum. The fine structure of this band (Figure 4) is in good agreement with the calculated germanium isotopic splitting of the Ge=O stretching mode in **1** (Table 3), closely resembling the band isotopic structures of this mode observed in GeO (Figure 4) and $F_2Ge{=}O$.[6] The suggested assignment to the Ge=O stretch in **1** of the band, observed in the 940−949 cm^{-1} range, provides a revision of the assignment to this mode of the band at 972 cm^{-1}, given in a preliminary report,[13a] which was not attributed to **1** in the present work.

The observed bands at 857.4, 794.8 and 770.7 cm^{-1} were assigned to the CH_3 rocking modes, since they are located in the 750−875 cm^{-1} region where the CH_3 rocking modes in methylgermanes are normally found.[37] These assignments also agree with the calculated harmonic frequencies of 860, 788, and 768 cm^{-1}, which, according to computed PED values, show a dominant contribution from the CH_3 rocking motions (Table 1).

The absorption in the 603−609 cm^{-1} spectral region shows a clear fine structure (Figure 4) in accord with the natural content of germaniun isotopes and in agreement with the calculations (Table 3) and was attributed to the antisymmetric ν_7 Ge−C stretch. This assignment also agrees with the location of this mode in the IR spectrum of dimethylgermathione, $(CH_3)_2Ge{=}S$, where it was found at 606 cm^{-1}.[38] The band of the

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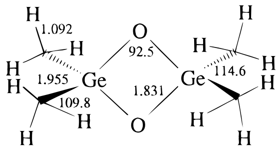

Figure 7. Optimized geometry of 1,3-cyclodigermoxane **6**.

symmetric ν_6 Ge−C stretch in **1** was not observed, which is likely due to a very low intensity of this fundamental, predicted to be about 10 times weaker than the antisymmetric Ge−C stretch (Table 1).

Ge═O Force Constant and Bond Order. The force constants of the Ge═O bond are calculated to be 7.04 mdyn/Å in **1** and 7.19 mdyn/Å in **5**. These values are close to that in $F_2Ge{=}O$ (7.43 mdyn/Å)[6] and are substantially higher than the force constant of the Ge−O single bond (~3.4−3.6 mdyn/Å), indicating strong π-bonding between Ge and O atoms in **1** and **5**.

The orders of these bonds have been estimated by the application of Siebert's empirical rule, which yielded values of 1.72 for **1** and 1.75 for **5**. These bond orders are lower than the Ge═O bond order in the $F_2Ge{=}O$ molecule (1.80).[6] This is consistent with the higher frequency of the Ge═O stretching mode in this germanone (989.9 cm^{-1})[6] in comparison to those observed in **1** and **5**,[7] 943.0 and 961.9 cm^{-1}, respectively.

1,1,3,3-Tetramethyl-1,3-cyclodigermoxane (6). The B3LYP-optimized planar (D_{2h}) structure of **6** is given in Figure 7. The predicted geometry for **6**, having methyl substituents at germanium, shows little difference from the structures of 1,3-cyclodigermoxanes stabilized by bulky aryl substituents, in which the four-membered OGeOGe ring is only slightly puckered, as established by X-ray diffraction.[43] The calculated Ge−O and exocyclic Ge−C bond lengths (1.831 and 1.955 Å) and GeOGe valence angle (92.5°) in **6** are close to those determined for the stable analogues[43] (1.814−1.820 and 1.951−1.956 Å and 92.1°, respectively).

The calculated harmonic vibrational frequencies and infrared intensities as well as suggested normal mode assignments in **6**, done with the help of vibration visualization, are given in Table 2. At the density functional B3LYP level of theory the OGeO in-plane stretching mode is predicted to be of very high intensity and to be found in the IR spectra at 665 cm^{-1}. The only observed strong band at 676.5 cm^{-1} in this region provides the best match to this predicted value, since the other closely lying bands are predicted to be much weaker (Table 2). The calculations predict the CH_3 rocking modes of b_{2u}, b_{1u}, and b_{3u} symmetry in **6** to be found at 773, 842 and 849 cm^{-1}, respectively, and to show comparable intensities. The observed band at 819.2 cm^{-1} can probably be attributed to any of these modes. However, the assignment of this band to the b_{3u} mode seems most likely, since the oscillator strength of this mode was calculated to be higher than for the two other modes.

Conclusion

In the present work we have directly observed the IR spectral features of the transient organic germanone **1**, generated by vacuum pyrolysis from the three independent precursors **2**−**4** and physically trapped in solid argon matrixes at 12 K. This observation, when compared with the previous preliminary report,[13] includes a revision of the assignment of the Ge═O stretching mode in **1**, found in the present study in the 940−949 cm^{-1} spectral region and exhibiting a clear band isotopic structure due to the natural abundance of germanium. The frequency of the Ge═O stretch in **1** is red-shifted by approximately 19 cm^{-1} with respect to that in parent germanone **5**, which is opposite to the Si═O stretching frequency change in related silanones.

Vacuum pyrolyses of epoxides **2** and **3** yield another transient molecule, the germene $(CH_3)_2Ge{=}CH_2$ (**9**), and stable byproducts, such as acrolein and isopropenyl methyl ketone, respectively, which have not been observed in the earlier thermal decomposition studies.[14] This provides evidence for a new thermal dissociation route in the germaepoxy derivatives **2** and **3**. We believe this results from the higher decomposition temperatures required for the precursor with a much shorter residence time in a vacuum reactor. These conditions facilitate two parallel $4 \rightarrow 2 + 2$ cycloreversion pathways for the 1,2-germaoxetanes, formed as primary intermediates in the pyrolyses of **2** and **3**.

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