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Kinetics and Mechanism of the Thermal Decomposition of 1,1-Dimethylgermetane

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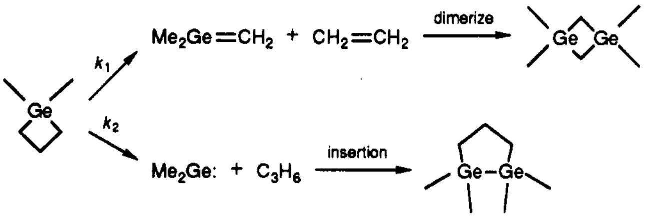
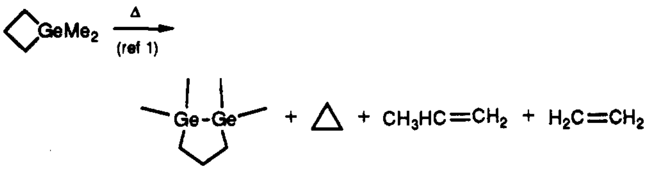
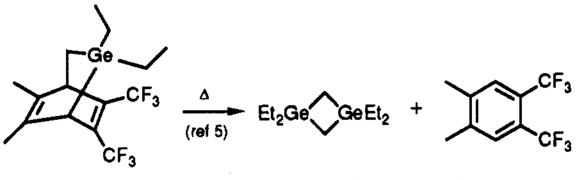
The gas-phase unimolecular decomposition of 1,1-dimethylgermetane has been investigated over the temperature range 683.9–751.2 K at pressures of ca. 15 Torr. Four products, cyclopropane, propene, ethene, and 1,1,2,2-tetramethylgermacyclopentane, are formed. Arrhenius parameters for the primary decomposition channels to (1) 1,1-dimethylgermene and ethene and (2) dimethylgermylene, cyclopropane, and propene are reported: (1) $\log k_1/\mathrm{s}^{-1} = 14.7 \pm 0.4 - 63.1 \pm 1.2\ \mathrm{kcal\ mol^{-1}}/RT \ln 10$; (2) $\log k_2/\mathrm{s}^{-1} = 14.1 \pm 0.3 - 60.7 \pm 0.8\ \mathrm{kcal\ mol^{-1}}/RT \ln 10$.



The surprisingly high activation energy for the 2 + 2 cycloreversion is interpreted in terms of a strong Ge–C bond dissociation enthalpy and/or reduced ring strain in the germetane.

In 1970, Gusel'nikov and co-workers demonstrated that the thermal fragmentation of 1,1-dimethylgermetane in the gas phase[1] differed significantly from the pyrolysis of its silicon and carbon analogues. Examples of these basic differences included formation of sizeable quantities of cyclopropane, propene, and 1,2-digermacyclopentane via processes without precedent in organosilicon[2] and hydrocarbon reactions.[3] Ethene formation was reported but dimerization of the implied germene,[4] a reaction subsequently reported by Barton[5] from pyrolysis of a bicyclic germene precursor, was not mentioned.





Formation of cyclopropane and 1,1,2,2-digermacyclopentane is also unusual and suggests the insertion of dimethylgermylene[6] into the strained germanium–carbon bond of the dimethylgermetane.[1] A kinetic and mechanistic study of these atypical reaction pathways for the thermal decomposition of 1,1-dimethylgermetane can provide information about the germanium–carbon bond enthalpy and strain energy of the germetane ring. Presently such information is sparse,[7] and an Arrhenius study of the small germacycle would be a valuable source of thermochemical data.[8]

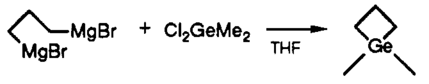
Table I. Products (%) from Pyrolysis of 1 in an Equimolar Amount of Butadiene at 770 K

	compd						
time (min)	2	3	4	5	6	7	5/7
35	20.4	17.8	12.5	2.6	24.4	22.3	0.12
70	23.5	16.1	14.4	1.8	24.6	19.6	0.09

Table II. Products (%) from Pyrolysis of 1 in a 4.5 Molar Excess of Butadiene at 770 K

	compd						
time (min)	2	3	4	5	6	7	5/7
35	22.7	20.6	10.8	10.3	24.2	11.4	0.90
70	26.3	18.4	11.4	7.6	23.8	12.5	0.61

The multistep synthesis of the dimethylgermetane reported by Mazerolles, Dubac and Lesbre[9] has been simplified to one high-yield step by the procedure described by Bickelhaupt and co-workers[10] in which dichlorodimethylgermane was added to a dilute solution of the 1,3-di-Grignard reagent produced from 1,3-dibromopropane.



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[1] Nametkin, N. S.; Gusel'nikov, L. E.; Ushakova, R. L.; Orlov, V. Yu.; Kuz'min, O. V. *Dokl. Akad. Nauk SSSR* **1970,** *194,* 741.

[2] Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B.* **1968,** 419.

[3] For a review of mechanisms of thermal hydrocarbon reactions, see: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.

[4] Multiply bonded germanium species have recently been reviewed: Barrau, J.; Escudie, J.; Satge, J. *Chem. Rev.* **1990,** *90,* 283. For a recent review of syntheses of theoretically intriguing structures consisting of Si, Ge, and Sn, see: Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 902.

[5] Barton, T. J.; Kline, E. A.; Garvey, P. M. *J. Am. Chem. Soc.* **1973,** *95,* 3078.

[6] The chemistry of divalent germanium (germylene) has recently been reviewed: Neumann, W. P. *Chem. Rev.* **1991,** *91,* 311.

[7] Pedley, J. B.; Rylance, J.; Sussex, N. P. L. *Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex: Sussex, U.K., 1977.

[8] Pseudo-first-order kinetic studies of the decomposition of 7-germabenzonorbornadienes have shown that the bicyclic germane is a unimolecular source of dimethylgermylene: Shusterman, A. J.; Landrum, B. E.; Miller, R. L. *Organometallics* **1989,** *8,* 1851.

[9] (a) Mazerolles, P.; Lesbre, M. *C. R. Acad. Sci. C* **1965,** *260,* 233. (b) Mazerolles, P.; Dubac, J.; Lesbre, M. *J. Organomet. Chem.* **1966,** *5,* 35.

[10] (a) Seetz, J. W. F. L.; Van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1984,** *277,* 319. (b) Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 990.

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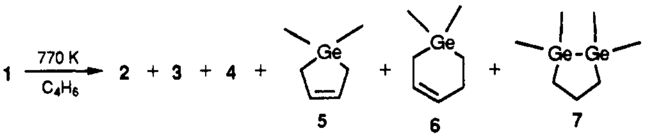
Results

Preliminary Trapping Studies. Vacuum flow pyrolysis of 1,1-dimethylgermetane (1) in the presence of a 10-fold excess of butadiene at 770 K (10% decomposition) afforded sufficient quantities of products to allow spectroscopic characterization of those containing germanium and chromatographic identification (by coinjection on two different columns) of the volatile hydrocarbons products. The following products were found (% yield): ethene, 2 (17); propene, 3 (16); cyclopropane, 4 (12); 1,1-dimethylgermacyclopent-3-ene, 5 (17); 1,1-dimethylgermacyclohex-3-ene, 6 (34); 1,2-digermacyclopentane, 7 (16).



Attempts to trap dimethylgermylene (8) and dimethylgermene (9) transients in a 20-fold excess of ethyne from a flow pyrolysis of 1 at 770–870 were unsuccessful.[11] The product distribution in the experiments with ethyne was similar to that observed in the neat flow pyrolysis of 1 at the same temperature. Noteworthy in both the neat and the C_2H_2 copyrolyses was the formation of 1,1,3,3-tetramethyl-1,3-digermetane (10) (4% in both experiments) from dimerization of 9 as well as the hydrocarbons 2–4.

Static pyrolyses of 1 with two different concentrations of butadiene, carried out at 770 K, complemented the flow experiments. The relative amounts of volatile hydrocarbon products showed very little change due to butadiene (Tables I and II) but the ratio of germacyclopent-3-ene to digermacyclopentane, 5/7, increased from 0.12 to 0.9 as the ratio of diene to germetane increased from 1:1 to 4.5:1. Since both germylene products are reasonably stable over this time, the greater yield of 7 from insertion into the Ge–C σ bond in both experiments suggests that the germetane is significantly more reactive (in terms of product formation) than the π system of the diene.[12]

Formation of cyclopropane from the unimolecular decomposition of a four-membered ring is not a common event,[13] and we explored the possibility that secondary decomposition of digermacyclopentane 7 was a major source of cyclopropane. That possibility has been eliminated as static pyrolysis of 7 at 772 K for 4 h afforded only 21% decomposition and provided a mixture of products: 1 (5%), 2 (1), 3 (10), 4 (1), and allyldimethylgermane (4). Cyclopropane was but a minor component in the pyrolysis of 7. Also indicative of the unimportance of secondary decomposition of 7 was the absence of allyldimethylgermane from the pyrolysis of the germetane.

In order to investigate the possibility that vibrationally excited cyclopropane was a source of propene, 14 Torr of cyclopropane (4) was subjected to static pyrolysis with several hundred Torr of added Ar as a bath gas. Again, propene was formed but in lower amounts than detected in the absence of the bath gas. For example, the ratios of cyclopropane/propene without added Ar were close to unity thoughout most of this work, but with added Ar, the ratio increased to 2.1 at 308 Torr of Ar. The extent to which the elimination of Me_2Ge: produces a vibrationally excited cyclopropane ring depends critically on the heat of formation of dimethylgermylene, an unknwon quantity.[14] For simplicity in the kinetic analysis and also the difficulty in achieving the necessary conformation for a concerted fragmentation of a germetane to propene and dimethylgermylene, we have considered formation of both C_3H_6 fragments together.

Scheme I

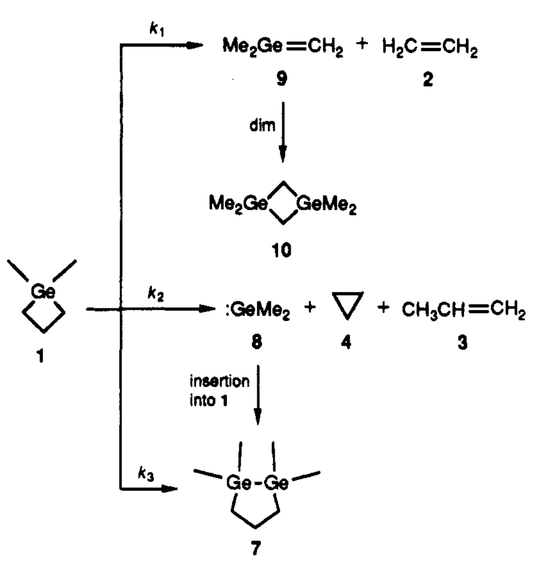


Table III. Change in Concentration of 1 with Time at 716.7 K

time (s)	unreacted 1 (%)	time (s)	unreacted 1 (%)
800	91.4	2000	80.3
1200	88.0	2400	76.0
1600	84.2	2800	72.4

Kinetics. a. Thermal Decomposition of Dimethylgermetane (1). Our preliminary product studies support the general Scheme I for the fragmentation of dimethylgermetane (1) suggested by Gusel'nikov.[1] Since the starting material, dimethylgermetane, was removed during the reaction by three independent pathways shown in Scheme I [(1) fragmentation to dimethylgermene (9) and ethene; (2) fragmentation to dimethylgermylene (8), cyclopropane, and propene; (3) insertion of 8 into the Ge–C bond of the germetane], the rate of disappearance of 1 is

$$-d[1]/dt = k_1[1] + k_2[1] + k_3[8][1] \qquad (1)$$

Applying the steady-state approximation to dimethylgermylene (8) yields

$$d[8]/dt = k_2[1] - k_3[1][8] = 0 \qquad (2)$$

$[8] = k_2/k_3$, and with substitution and rearrangement:

$$-d[1]/dt = (k_1 + 2k_2)[1] = k_{obs}[1] \qquad (3)$$

$$k_{obs} = k_1 + 2k_2$$

The slope of a plot of ln [1] against time (t) (Table III) affords k_{obs}, the observed rate constant for the disap-

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[11] Nefedov, O. M.; Ergorov, M. P.; Kolesnikov, S. P. *Sov. Sci. Rev. B Chem.* **1988**, *12*, 53.

[12] Photochemically generated Me_2Si: in solution also inserts into the germanium–carbon bond of 1 at room temperature: Namavari, M.; Conlin, R. T. Unpublished results.

[13] A variety of transition metallacyclobutanes are known to eliminate cyclopropane: Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

[14] Heats of formation for transient divalent molecules typically run a controversial course with theory and even within the experimental interpretation. For a recent version of the tortuous evolution for ΔH_f of $:SiR_2$, see: O'Neal, H. E., Ring, M. A.; Richardson, W. H.; Licciardi, G. F. *Organometallics* **1989**, *8*, 1968. Walsh, R. *Organometallics* **1989**, *8*, 1973. Gordon, M. S.; Boatz, J. A. *Organometallics* **1989**, *8*, 1978. More recently, see: Pilcher, G.; Luisa, M.; Leitao, P.; Yang, M.-Y.; Walsh, R. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 841. Nevertheless, on the basis of thermochemical estimates, it appears unlikely that elimination of dimethylgermylene produces thermally excited cyclopropane: Walsh, R. Personal communication.

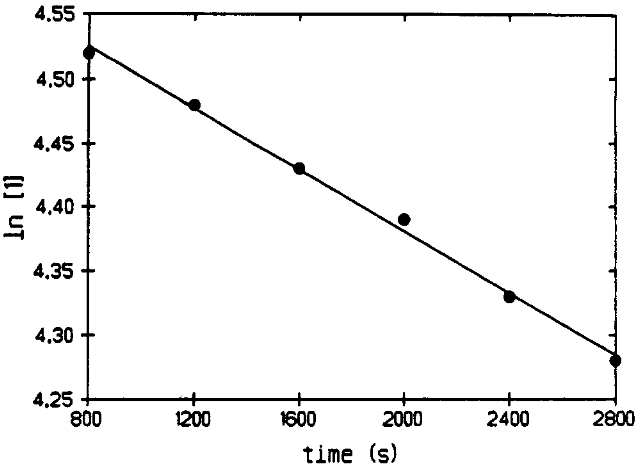


Figure 1. Plot of the change in concentration of 1 with time at 716.7 K.

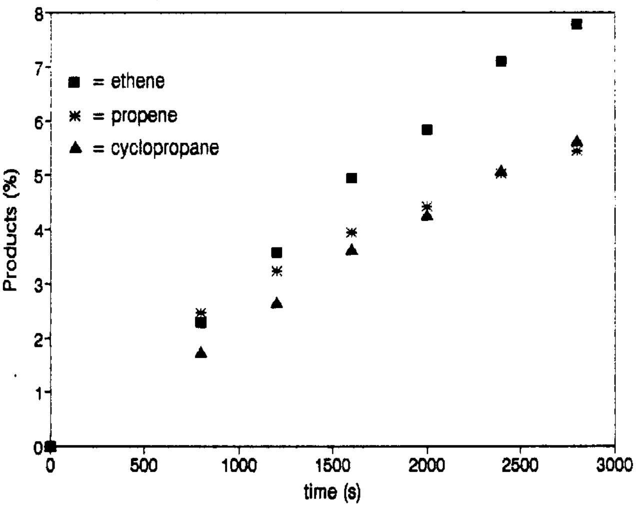


Figure 2. Time dependence for hydrocarbon products 2–4 at 716.7 K.

Table IV. Time Dependence for Hydrocarbon Products 2–4 at 716.7 K[a]

	compd			
t (s)	2	3	4	3 + 4
800	2.30	2.46	1.73	4.19
1200	3.58	3.22	2.65	5.87
1600	4.93	3.94	3.62	7.56
2000	5.82	4.41	4.26	8.67
2400	7.10	5.03	5.08	10.11
2800	7.79	5.43	5.63	11.06

[a] $[2]/([3] + [4]) = k_1/k_2$.

pearance of 1. A plot of ln [1] against time (Figure 1) provided a straight line whose slope is the rate constant, $k_{obs} = (1.183 \pm .04) \times 10^{-4}$ s^{-1}, for decomposition of the germetane. This value of the rate constant for disappearance of the germetane is enhanced by the very efficient gas-phase reaction of dimethylgermylene.

b. Kinetics of Product Formation. Characterization of the reaction products 2–4 and their time dependence (see Table IV) allows an internal check that k_{obs} indeed corresponds to the formation of the chromatographically observed products. The time evolution of the product distribution at 716.7 is shown in Figure 2.

In Table IV, the time dependence for the fragmentation of starting material is shown at 716.7 K (a typical static pyrolysis temperature). Table V provides the time dependence of product formation, 2 and (3 + 4), at 716.7 K.

Table V.[a] **Rate Constants (×10^5) for k_1, k_2, and k_f (s^{-1})**

T (K)	k_1	k_2	k_f	k_2/k_1
683.9	0.375	0.498	0.873	1.33
689.9	0.528	0.686	1.214	1.30
698.4	0.846	1.332	2.178	1.58
706.6	1.573	2.178	3.751	1.38
716.7	3.405	4.212	7.617	1.23
721.5	4.421	5.466	9.887	1.24
728.9	6.766	8.267	15.03	1.22
737.4	9.747	11.99	21.73	1.23
743.6	15.11	18.02	33.13	1.19
751.2	21.86	26.82	48.68	1.22

[a] $k_f = k_1 + k_2$.

Table VI. Arrhenius and/or Eyring Parameters for k_f, k_1, and k_2

$\log k_f/\mathrm{s}^{-1} = 14.7 \pm 0.3 - 61.7 \pm 0.8/RT \ln 10$
$\log k_1/\mathrm{s}^{-1} = 14.7 \pm 0.4 - 63.1 \pm 1.2/RT \ln 10$
$\Delta H^{\ddagger} = 61.6 \pm 1.2$ kcal/mol, $\Delta S^{\ddagger} = 5.0 \pm 1.6$ cal/(mol deg)
$\log k_2/\mathrm{s}^{-1} = 14.1 \pm 0.3 - 60.7 \pm 0.8/RT \ln 10$
$\Delta H^{\ddagger} = 59.2 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = 2.2 \pm 1.1$ cal/(mol deg)

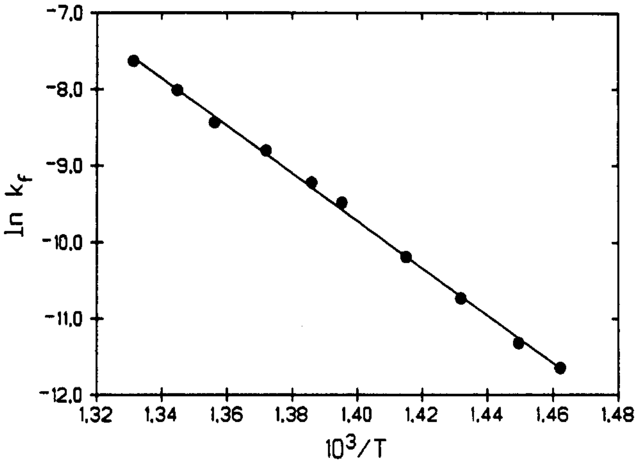


Figure 3. Arrhenius plot of ln k_f vs $10^3/T$.

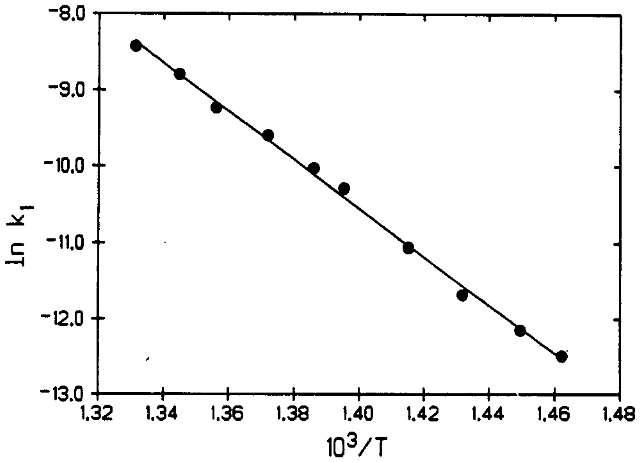


Figure 4. Arrhenius plot of ln k_1 vs $10^3/T$.

Plots for the fragmentation of 1, k_f, and for the formation of 2, k_1, and (3 + 4), k_2, in Figures 3–5 gave Arrhenius terms. Arrhenius and Eyring parameters are listed in Table VI.

Discussion

There are relatively little data pertinent to the dissociation enthalpy of germanium–carbon bonds, a value

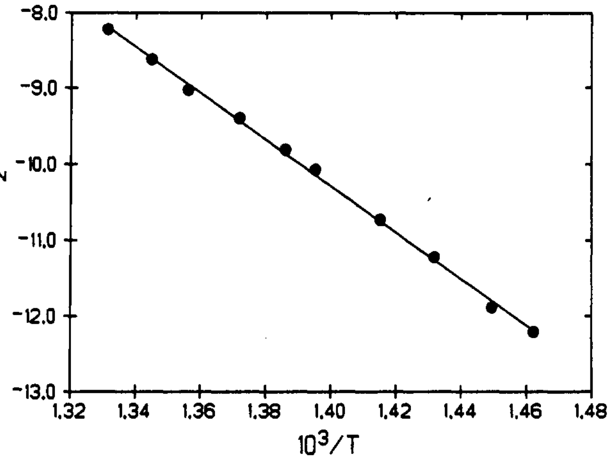
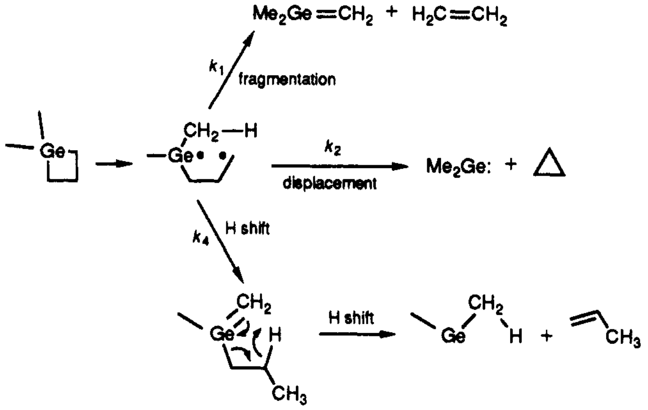


Figure 5. Arrhenius plot of ln k_2 vs $10^3/T$.

which is critically important to the interpretation of this work.[15] The pattern of reports has shown that earlier measures of the so-called Ge–C bond strength have likely been underestimated. For example, values of the bond dissociation enthalpy have steadily increased. Among the previous estimates of the Ge–Me bond energy for tetramethylgermane are the following: 76,[16] 77.0,[17] and 83 kcal/mol.[18] Although the range of quoted error limits is not unreasonable for the three different types of physical measurements (±5%), the highest value, 83 kcal/mol, is the one in best accord with the activation energy for fragmentation to ethene and dimethylgermene, $E_{act} = 63.1$ kcal/mol. A possible rationale for the surprisingly high E_a reported here (slightly greater than observed for cyclobutane and dimethylsiletane 2 + 2 cycloreversions) might be due to the compensating effects of the decreasing ring strain, E_s, and the lower germanium–carbon bond energy. In other words, an expected *increase* in E_a as a consequence of reduced ring strain might be offset by a *decrease* in the energy required to break such bonds.[19] For example, assuming the ring strain in the germetane to be $\approx$20 kcal mol^{-1},[20] the activation enthalpy for fragmentation to ethene and dimethylgermene from initial cleavage of the germanium–carbon bond may be estimated: $\Delta H° \approx D(\text{Ge–C}) - E_s = 83 - 20 = 63$ kcal/mol.

Scheme II



It is important to recognize that the site of initial ring opening remains uncertain and a case for carbon–carbon bond cleavage might also be made. An additional factor which influences the activation enthalpy of the 2 + 2 cycloreversion is the extent of delocalization of the electrons of the breaking bond by the germanium atom (germanium–carbon bond). In related mechanistic studies of thermal siletane decomposition, the dominant site of bond breaking is thought to occur at the C–C bond.[21] Since Si–C and C–C bond energies are quite similar, secondary influences such as stabilization of the carbon radical center β to Si tend to favor earlier C–C bond cleavage.[22] Although there are no gas-phase measurements of the magnitude of this stabilization for radical centers β to germanium, the phenomenon is well recognized in solution work.[23] From ESR studies, estimates of the β stabilization by germanium are larger than those measured for silicon.[24] Whether the magnitude of this effect for germanium is sufficiently large to divert the course of unimolecular ring opening of the germetane from path a (cleavage of the Ge–C bond) to path b (cleavage of the C–C bond) requires further study.

The mechanism for formation of cyclopropane and propene is problematical. At the outset of this work, we had considered the possibility that secondary decomposition of cyclopropane (4) was the source of propene in the reaction mixture. A maximum for the production of cyclopropane was not detected by chromatographic analysis at 6–8 different time intervals. The absence of such a maximum, however, does not exclude the possibility that vibrationally excited cyclopropane (4) is an intermediate in propene (3) formation but does suggest that secondary decomposition of 4 from its thermal ground state is not a significant path to propene in this work. This suggestion is supported by independent studies in which neat cyclopropane (100 Torr) was pyrolyzed at 716.7 K for 60 min and less than 3% isomerized to 3.[25] In comparison to fragmentation of the germetane, approximately equal amounts of 3 and 4 were produced at each sampling over a wide range of time and temperature.

The lower *A* factor for production of C_3H_6 and dimethylgermylene, log $A = 14.1$, suggests a "tighter" transition state than observed for the 2 + 2 cycloreversion to ethene and dimethylgermene. The activation barrier, 60.7 kcal/mol, however, shows none of the decrease that has usually been associated with single step (i.e. *concerted*) reactions. A similar anomaly has also been reported for the decomposition of cyclobutanone,[26] where the formation

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[15] In contrast to the current situation for Ge–C bonds, disociation enthalpies for the trialkygermanium–hydrogen bond appear to be converging around 82 kcal/mol: (a) Doncaster, A.; Walsh, R. *J. Phys. Chem.* **1979**, *83*, 568. (b) Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746.

[16] Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17.

[17] Dzarnoski, J.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kinet.* **1981**, *14*, 279.

[18] Smith, G. P.; Patrick, R. *Int. J. Chem. Kinet.* **1983**, *15*, 167.

[19] A commonly accepted view of most nonconcerted small-ring fragmentations is one in which the reaction is initiated by homolytic cleavage of the weakest ring bond. For a possible exception, see: Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1986**, *5*, 1205.

[20] Given that germanium–carbon bonds are longer than silicon–carbon bonds and E_s for siletanes is $\approx$22 kcal/mol,[21] this assumption appears quite reasonable.

[21] Barton, T. J.; Marquardt, G.; Kilgour, J. A. *J. Organomet. Chem.* **1975**, *85*, 317.

[22] Conlin, R. T.; Namavari, M.; Chickos, J. S.; Walsh, R. *Organometallics* **1989**, *8*, 168.

[23] Riviere, M.; Reviere-Baudet, M.; Satge, J. In *Comprehensive Organometallic Chemistry*; Pergamon: London, 1982; Vol. 2, p 415.

[24] Kawamura, T.; Meakin, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 8065.

[25] This is consistent with reported Arrhenius parameters for the unimolecular decomposition of cyclopropane in ref 3.

of cyclopropane and carbon monoxide display a relatively reduced *A* factor, log $A = 14.4$, but a relatively high value for E_a, 58.0 kcal/mol.[27]

Although a small surface enhancement on the rate of decomposition was detected in a packed reaction vessel, we note that such an effect if present for C_3H_6 formation might operate on a portion of the decomposition pathways and, hence, not appear obvious. For example, pyrolysis of 1 in a packed vessel, surface to volume ratio of 12 to 1, at 716.7 K provided a decomposition rate constant whose value was within 5% of that value obtained in an unpacked reaction vessel. Curiously the relative ratios of C_3 to C_2, however, exhibited a change which favored an increase from 1.82 to 2.37 in the unpacked and packed vessels, respectively. Although such a difference is usually associated with a surface catalyzed component to the reaction kinetics, the excellent first-order fit for the formation of the hydrocarbons in both reaction vessels as well as the relatively high activation barriers leads us to conclude that the significance of a heterogeneous component on the reaction kinetics, if present, is small. Furthermore, product ratios from the germene amd germylene intermediates in the flow system, conditions where surface catalysis is generally considered to be of minimal importance, were similar to those observed in the static pyrolysis.

Presently we have no simple explanation for the unimolecular formation of propene from 1, but a speculative pathway is considered in Scheme II. An attraction of the mechanistic Scheme II is that it accounts for propene production from a series of unimolecular events initiated by k_4. The final step leading to an alkene formation has precedent from previous gas-phase studies of alkylsilenes[28] and alkylsilylenes,[29] which thermally release alkenes. Although elimination of propene from the methylpropylgermene might also be anticipated, it is relevant that Barton et al. did not report the analogous formation of methylethylgermylene and ethene from trapping studies on 1,1-diethylgermene.[5] Furthermore, the key step of this alternative pathway for propene, k_4, requires the unusual thermal isomerization of a 1,4-biradical to methylpropylgermene.[30]

Formation of germacyclopent-3-enes by trapping dimethylgermylene from a variety of precursors[31] with butadiene is usually diagnostic for the presence of the divalent germanium. Nevertheless, the stereospecific production of the germacyclopent-3-enes[32] does not allow unambiguous distinction between two mechanistic possibilities for its formation. For example, both a cheleotropic 1,4-addition of the germylene to the diene or a sequence of stereospecific steps initiated by 1,2-addition to a single π bond followed by a thermally allowed antarafacial 1,3-sigmatropic shift[33] provide products with the same stereochemistry.

The facile insertion of dimethylgermylene into the Ge–C bond of the germetane draws precedent from earlier studies of the thermal decomposition of 7,7-dialkylgermanorbornadienes.[34] The products, a digermabicyclooctadiene and a naphthalene derivative, were believed to arise from elimination of dimethylgermylene which inserted into the Ge–C bond of the starting material, a germanorbornadiene. Such insertion reactions may involve complexation between the divalent germylene and its tetravalent precursor prior to insertion.[35]

Experimental Section

General Data. Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R24B 60-MHz spectrometer using methylene chloride as an external standard, and carbon NMR spectra were obtained on a JEOL FX 90Q spectrometer with D_2O or $CDCl_3$ as a lock solvent. Chemical shifts are reported in ppm downfield from external tetramethylsilane. Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. Low-resolution mass spectra were determined on a HP 5970A mass selective analyzer coupled to a HP 5790A gas chromatograph.

Pyrolysis kinetics were carried out in a 250-mL quartz vessel submerged in a molten-salt bath (eutectic mixture, 50% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3, mp 142 °C) that was insulated by Aqua-Cell (diatomite, Johns-Manville Co.). A Thermotrol Model 1053A (GCA Precision Scientific) proportional controller (230 V) with a Model 1183 platinum resistance temperature detector was used to control the temperature. A stainless steel mineral insulated heating element (Chromalox Comfort Conditioning Division) was used as a heating element. Temperature was measured by a Chromel-Alumel thermocouple (Type K) which was connected to a Leeds & Northrup Type K-3 potentiometer with a null detector (Leeds & Northrup, 9828 D.C.). Temperatures were constant to ±0.1 K. A thermocouple, held in the center of the molten-salt bath, was calibrated to a Brooklyn thermometer (range 298–355 °C). Vapors of 1,1-dimethylgermetane (1) were introduced into the quartz reaction vessel through a vacuum line. Initial pressures of 1 for kinetics were measured by a Model PDR-C-2 pressure gauge and Model 227 AHS-A-100 Baratron (MKS Instrument Co.).

Typically, each kinetic/pyrolysis run was sampled six times by removing a small portion of pyrolysate (≈1.5 Torr) from the reaction vessel. Two GC runs were used for each point in a rate constant, and at least six points were used for each rate constant plot. Rate constants and activation parameters were calculated by using the method of least squares. Low-pressure flow pyrolyses were done in a quartz reaction tube (10 mm i.d. × 30 cm) wrapped with nichrome ribbon, covered with asbestos tape, and attached to a high-vacuum line. The quartz tube was seasoned with hexamethyldisilazane before use. Residence times in the hot zone were tenths of seconds and pressures were 1–5 Torr. A constriction, 0.8 mm i.d., was placed at the end of the hot zone and

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[26] Numerous examples of CO elimination from a variety of substituted cyclobutanones have been reported. For a recent summary, see: Sponsler, M. B.; Dougherty, D. A. *J. Org. Chem.* **1984**, *49*, 4978.

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[30] A similar mechanistic hypothesis for isomerization of 1,4-biradicals has been considered has been questioned previously; see: Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1984**, *3*, 918.

[31] (a) In addition to the many examples listed in ref 6 is the thermal gas-phase α elimination from pentamethyldigermanes: Ma, E. C.-L.; Paquin, D. P.; Gaspar, P. P. *J. Chem. Soc., Chem. Commun.* **1980**, 381. (b) Photolysis of phenylpolygermanes: Mochida, K.; Kikkawa, K.; Nakadeira, Y. *Chem. Lett.* **1988**, 1089. Wakasa, M.; Yoneda, I.; Mochida, K. *J. Organomet. Chem.* **1989**, *366*, C1.

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[33] Photolysis of *trans*-2-methyl,3-(1-*trans*-propenyl)-1,1-dimesitylsilirane in solutions containing excess *trans,trans*-1,4-hexadiene yields *cis*-2,5-dimethyl-1,1-dimesitylsilacyclopent-3-ene stereospecifically: Zhang, S.; Conlin, R. T. *J. Am. Chem. Soc.* **1991**, *113*, 4272.

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used to control pressure and residence time.

Product yields from vacuum flow pyrolyses were based on the amount of decomposition of starting material 1 and determined chromatographically with predetermined response factors for the organogermane products. 1,1-Dimethylgermetane (1) was synthesized by a modified version of Bickelhaupt's method.[10] Tetramethylgermane was synthesized by the procedure used for tetramethyltin,[36] and dimethyldichlorogermane was synthesized by the method of Sakurai and Kumada.[37]

Low-Pressure Flow Pyrolysis of 1. Vapors from 0.6 g (4.1 mmol) of 1, at a rate of 100 mg/15 min, were pyrolyzed in a quartz tube at 826 K. The product mixture was separated into two fractions by trap to trap distillation of the reaction mixture with slush baths: dry-ice 2-propanol and toluene/liquid N_2 (−95 °C). Ethylene (2), propene (3), and cyclopropane (4) were gaseous products, while undecomposed 1, 1,1,3,3-tetramethyldigermetane (10), and 1,1,3,3-tetramethyl-1,3-digermacyclopentane (7) were the heavier germanium-containing products. Decomposition of 1 at 826 K was 54%, and 10 and 7 were formed in 3% and 35% yields, respectively. Preparative VPC of 10 and 7 was performed on a SF-96 column (20% on Chromosorb W, $^1/_4$ in. × 20 ft). ^{1}H and mass spectra of 1,[10] 7,[1] and 10[38] were identical to those reported earlier. Previously unreported ^{13}C NMR data are as follows. 1 (neat): δ −0.26 (s), 20.16 (t), 21.39 (t). 7 (neat): δ −3.97 (s), 20.55 (t), 24.45 (t). 10 (neat): δ 2.47 (s), 10.53 (t).

Static Pyrolysis of 1,1-Dimethylgermetane (1) with Butadiene. Static pyrolysis of 1 (7.2 Torr) and 1,3-butadiene (7.2 Torr) was carried out at 694 K in a fused salt bath. Aliquots of the reaction mixture were analyzed at 10-min intervals by GC on a SP-2100 column ($^1/_8$ in. × 12 ft). In addition to the products observed in the neat pyrolysis of 1, 1,1-dimethylgermacyclohex-3-ene (6) (24%) and 1,1-dimethylgermacyclopent-3-ene (5) (3%) were formed. A similar experiment, but with a different ratio of 1 (6.2 Torr) to 1,3-butadiene (27.9 Torr), was carried out at the same temperature (see Results).

Low-Pressure Flow Pyrolysis of 1,1-Dimethylgermetane (1) with Butadiene. Vapors from 0.4 g (2.8 mmol) of 1 were introduced at a rate of 75 mg/15 min in the presence of a 10-fold excess of 1,3-butadiene at 770 K. Decomposition of 1 was 10%, and the pyrolysate was concentrated by bulb-to-bulb distillation followed by preparative chromatography on an OV-17 column (20% on Chromosorb W 45/60, $^1/_4$ in. × 20 ft). Three germanium-containing products, 1,1-dimethylgermacyclopent-3-ene (5) (26%), 1,1-dimethylgermacyclohex-3-ene (6) (34%), and 1,1,2,2-tetramethyl-1,2-digermacyclopentane (7) (26%), were isolated.

Data for 5: ^{13}C NMR (neat) δ −2.73 (g), 18.66 (t), 130.77 (d); ^{1}H NMR, IR, and mass spectral data agree with previously reported values.[29]

Data for 6: ^{13}C NMR (neat) δ −3.25 (s), 11.31 (t), 13.20 (t), 22.56 (t), 127.13 (d), 129.93 (d); ^{1}H NMR (neat) δ 0.14 (6 H, s, CH_3Ge), 0.73 (2 H, t, J = 6.4 Hz, CCH_2Ge), 1.32 (2 H, app d, J = 4.2 Hz, $C{=}CCH_2Ge$), 2.18 (2 H, m, $GeCCH_2$), 5.71 (2 H, m, $CH{=}CH$); mass spectral data agree with previously reported values.[39]

Low-Pressure Flow Pyrolysis of 1 with Acetylene. Pyrolysis of vapors from 0.5 g (3.5 mmol) of 1 with a 20-fold excess of acetylene was carried out at 500–600 °C. The same products as observed from the neat pyrolysis case were obtained; however, no products corresponding to acetylene adducts were found. A possible implication of this result is that the stained germirene and germetene are formed reversibly.

Pyrolysis Kinetics. Kinetics were carried out in the vapor phase over the temperature range 690–751.3 K at pressure near 14 Torr in a fused-salt bath. GC analysis of aliquots (≈1.5 Torr) of the pyrolysis mixture at each reaction time was done on a SP-2100 column ($^1/_8$ in. × 12 ft). Rate constants for the fragmentation of 1,1-dimethylgermentane (1) and for the formation of 2 and (3 + 4) are summarized in Table V.

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