methylene (**3**). The symmetry breaking entails rotation and inversion of one methylene group, passing over a C_1 transition state (**9**), crossing the C_s symmetric disrotation coordinate, and inverting the second methylene via another transition state of structure **9**, before rejoining the C_2 conrotatory pathway. The reaction pathway for single rotation also breaks symmetry to avoid C_s (0,90)-trimethylene (**4**), and passes through a single transition state (**10**) of C_1 symmetry.

We have used the highest energy transition state **9** on the pathway for two-center rotation to calculate the α and β deuterium isotope effects on double rotation. Both α and β isotope effects at 422.5 °C are calculated to be moderate and normal, with the β H/D isotope effects much smaller than the α effects. In cyclopropane-*1,2*-$^2H_2$ (**1**), these individual isotope effects give rise to a calculated overall kinetic preference of $z_{12} = 1.13$ for C(1)–C(3) (or C(2)–C(3)) over C(1)–C(2) coupled rotation. This value of z_{12} is quite close to that assumed by Berson and coworkers[12] in their original analysis of the stereomutations of **1**.

Our calculated value $z_{12} = 1.13$ for **1** is very different from the value of about $z_{12} = 0.4$ that is necessary for the result obtained by Baldwin[16] for cyclopropane-*1*-^{13}C-*1,2,3*-$^2H_3$ (**2**) to be compatible with the results obtained both by Berson[12] and by Baldwin[15] for **1**. Our calculations do find that the difference in isotopic substitution between **1** and **2** should alter the relative contributions of the single and double methylene group rotation mechanisms in these two cyclopropanes, but the effect is computed to be small, amounting only to about a 10% difference in the ratios of the rates for single and double rotation. On the basis of these computational findings, we conclude that there is no apparent way to reconcile the experimental results obtained for **1**, which indicate a clear preference for double rotation, with those obtained for **2**, which indicate that single and double methylene group rotations proceed at essentially equal rates.

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Supplementary Material Available: Complete GVB/6-31G* optimized geometries and vibrational frequencies for **3**–**10** and results of calculations of isotope effects on ratios of microscopic rate constants (23 pages). Ordering information is given on any current masthead page.

Three-Membered Rings of Carbon, Silicon, and Germanium: An Analysis of Thermodynamic Stability to Fragmentation

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Abstract: Ab initio quantum mechanical methods have been used to determine the strain energies of all possible saturated three-membered rings, c-$XH_2YH_2ZH_2$, and the energetics of the decomposition reactions c-$XH_2YH_2ZH_2 \rightarrow$:XH_2 + $H_2Y{=}ZH_2$ for X, Y, Z = C, Si, Ge. The three-membered-ring (3MR) decomposition enthalpy can be semiquantitatively predicted from a simple model using the strain energies along with published single bond dissociation energies, π-bond energies, and divalent state stabilization energies. Of the ten rings studied, germirane (c-$GeH_2CH_2CH_2$) is by far the least stable with respect to dissociation, being only about 20 kcal/mol more stable than GeH_2 + $H_2C{=}CH_2$. Thus the lack of success of experimental efforts to form a germirane has a thermochemical origin. This observation also helps account for observed differences in methylene, silylene, and germylene addition reactions to dienes. The estimation of substituent effects on ring decomposition enthalpies is facilitated by this model.

Introduction

In recent years the three-membered rings comprising group 14 elements have received considerable attention.[1-6] Small-ring compounds seem to be inherently and enduringly interesting to chemists, due in large part to their high strain, novel ring bonding, and, in the case of group 14 cyclotrimetallanes, reactive bonds between heavy atoms (e.g. Si–Ge). The group 14 cyclotrimetallanes are not only interesting, they are also synthetically useful as convenient sources of highly reactive carbene-like species and dimetallenes, because they decompose photolytically via the reaction

$$\text{c-}XR_2YR_2ZR_2 \rightarrow :XR_2 + R_2Y{=}ZR_2 \qquad (1)$$

where X, Y, Z = group 14 elements.[2,3] In some cases thermolysis yields the same products.[3,4,7,8]

Of the ten cyclotrimetallane rings made up of C, Si, and Ge, all have been synthesized to date except the three which contain a single Ge atom. Among the latter group the germirane (GeC_2) ring is especially notable for its elusiveness. Germiranes have been

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proposed as intermediates in several reactions but have never been detected,[9] and an attempt to synthesize a germirane by reacting diazomethane with a germene has been unsuccessful.[10] Other group 14 cyclotrimetallanes have been synthesized via reactions analogous to diazomethane addition to germene, suggesting that the enthalpy change associated with reaction 1 may be significantly lower for germirane than for other three-membered rings.

Qualitative reasons for the differing stabilities of cyclotrimetallane rings with respect to decomposition via reaction 1 may be understood by examining the various contributions to the enthalpy change of this reaction. Consider, for example, the decomposition of silacyclopropane, c-SiC_2H_6, to silylene, SiH_2, and ethylene, C_2H_4. The strengths of the Si–C bonds, the strength of the C–C π-bond, and the ring strain enthalpy are the obvious contributors to $\Delta H(1)$. Thus, because Si–C and C–C single bonds have nearly the same strength (within 2 kcal mol^{-1}),[11] the decomposition of silacyclopropane is correctly predicted to be less endothermic than that of cyclopropane due to the higher strain enthalpy of the silacyclopropane ring.[6] However, this cursory analysis is *quantitatively* flawed. Boatz and Gordon[6] found that ΔH_0 for the decomposition of c-SiC_2H_6 to SiH_2 and C_2H_4 is ca. 55 kcal mol^{-1} less than ΔH_0 for the production of C_2H_4 and singlet CH_2 from cyclopropane, but they also found that the ring strain of silacyclopropane exceeds that of cyclopropane by no more than 14 kcal mol^{-1}. Thus, we are left with a difference of about 40 kcal mol^{-1} between the reaction enthalpies for which there is no accounting!

Here we present the results of ab initio quantum mechanical determinations of the strain enthalpies[12] of the ten cyclotrimetallanes, c-$XH_2YH_2ZH_2$, composed of C, Si, and Ge atoms and the energetics of decomposition of these compounds via reaction 1. We will show that the decomposition enthalpies can be predicted semiquantitatively from a simple model which expresses the enthalpy of reaction 1 in terms of contributions from single bond dissociation enthalpies (BDE's),[12] strain enthalpy, π-bond enthalpy, and Walsh's so-called divalent state stabilization energy (DSSE).[11] It is the DSSE which accounts for most of the 55 kcal mol^{-1} difference between the cyclopropane and silirane decomposition enthalpies mentioned above. Germirane is, by far, the least stable ring with respect to dissociation via reaction 1. The analysis of the enthalpy of decomposition in terms of the simpler component enthalpies allows for ready estimation of the effects of substituents on this reaction from known substituent effects on the individual components.

Ab Initio Quantum Mechanical Methods

Molecular electronic energies were determined by optimizing structures using restricted Hartree-Fock self-consistent-field (SCF) analytic gradient techniques.[13] Residual Cartesian and internal coordinate gradients did not exceed 10^{-6} au. Analytic second derivative methods[14] were used to evaluate the quadratic force constants and resulting harmonic vibrational frequencies at the SCF level. For the XH_2 molecules optimizations were carried out on the lowest singlet states.

Our basis set is of double-ζ plus polarization quality for heavy atoms and double-ζ for hydrogen, which is therefore designated DZ+d. Specifically, for carbon and silicon the Huzinaga–Dunning[15] (9s5p/4s2p) and (11s7p/6s4p) sets were augmented with Cartesian polarization functions with exponents $\alpha_d(C) = 0.75$ and $\alpha_d(Si) = 0.50$. The hydrogen basis is the Huzinaga–Dunning[15] (4s/2s) set. The germanium basis set is a 7s5p2d segmented contraction[16] of Dunning's 14s11p5d primitive set,[17] to which we have appended an additional polarization d-function [$\alpha_d(Ge) = 0.25$]. Thus, the germanium basis set is (14s11p6d/7s5p3d). Similarly constructed basis sets[16,17] for the neighboring atoms gallium and arsenic yield excellent results for geometries and isomeric energy differences when compared to more flexibly contracted basis sets obtained from the same primitive basis set.[18]

Reaction enthalpies at 0 K were evaluated by adding to the difference in electronic energies of reactants and products, ΔE_{elec}, the difference in SCF zero-point harmonic vibrational energies (ΔZPVE) multiplied by a scale factor of 0.91. This scale factor provides an approximate correction for the overestimation of zero-point vibrational energies by the SCF method.[19] To include the effects of electron correlation in estimates of the reaction enthalpies, we employed the size-extensive coupled cluster singles and doubles method (CCSD).[20] The CCSD electronic energy of each molecule was evaluated at its SCF-optimized geometry, with all corelike (C 1s; Si 1s, 2s, 2p; Ge-1s, 2s, 2p, 3s, 3p, 3d) orbitals kept frozen.

We determined ab initio strain enthalpies using homodesmotic reactions.[21] It has been shown that when adequate basis sets and correlated levels of theory are employed, computed heats of homodesmotic reactions agree with experimental values to within a few kcal mol^{-1}.[6,22] Because there has been some variation in the ways different authors have applied homodesmotic reactions to nonhydrocarbons, we state our approach here. George et al.[21] defined a homodesmotic reaction of hydrocarbons as one which conserves the number of C–C bonds of each type (sp^3–sp^3, sp^3–sp^2, etc.) and the number of groups of each type. Here the word "group" has Benson's meaning: a polyvalent atom together with all of its neighboring atoms.[23] George et al. did not speak explicitly of Benson's groups, but that is the essence of their definition,[21] and paraphrasing it in terms of groups facilitates its extension to nonhydrocarbons. For example, the strain enthalpy[12] of silacyclopropane is here taken to be the enthalpy change of the reaction

$$CH_3SiH_2CH_3 + 2SiH_3CH_2CH_3 \rightarrow \text{c-}SiH_2CH_2CH_2 + 2SiH_3CH_3 + CH_3CH_3. \quad (2)$$

Note that in reaction 2 the numbers of Si–$(C)_2(H)_2$, Si–(C)$(H)_3$, C–(Si)$(H)_3$, C–(C)(Si)$(H)_2$, and C–(C)$(H)_3$ groups (Benson's notation[23]) are conserved.

Thermochemical Analysis

A semiquantitative expression for the enthalpy of reaction 1 in terms of the factors (bond enthalpies, strain, etc.) which contribute to it can be deduced by imagining carrying out the reaction in several distinct steps. Consider the decomposition of silacyclopropane, c-$SiH_2CH_2CH_2$, to silylene, SiH_2, and ethylene. If in the first step a Si–C bond is broken to produce $\dot{Si}H_2CH_2\dot{C}H_2$, then a zeroth-order approximation to the corresponding enthalpy

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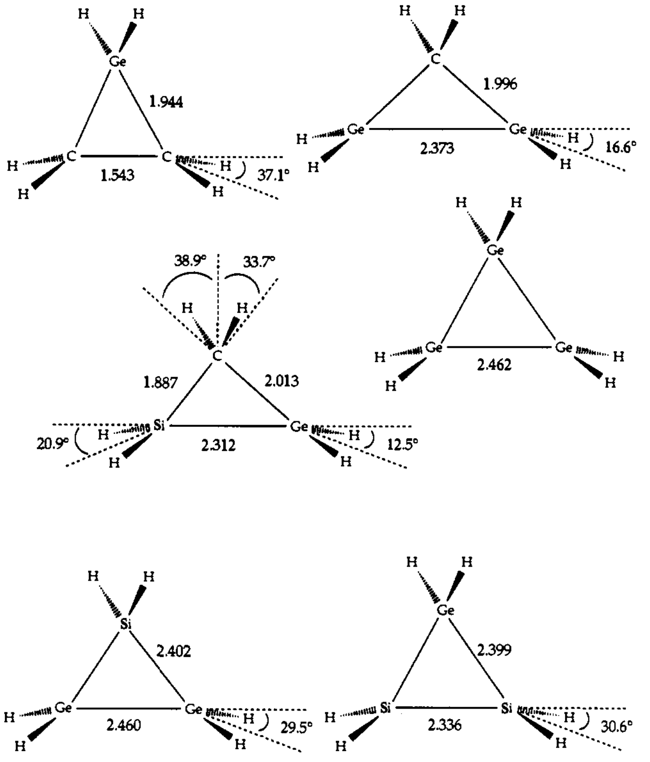

Figure 1. Self-consistent-field (SCF) optimized geometries of the germanium-containing rings investigated in this research. The basis set is of double-ζ plus d (DZ+d) quality. The angles shown are between the H_2M bisector and the extension of the bond between the heavy atoms. Bond distances are in angstroms.

change is the dissociation enthalpy of the SiH_3-CH_3 bond minus the strain enthalpy (because breaking the bond relieves the ring strain). Breaking the second Si-C bond to form SiH_2 and C_2H_4 actually requires less than the SiH_3-CH_3 BDE for two reasons: (1) the dissociation of the second Si-C bond is accompanied by the formation of a C-C π bond, and (2) the breaking bond is more similar to a $\dot{S}iH_2-CH_3$ bond than to SiH_3-CH_3, and in general a bond to a silylene group ($R'-\dot{S}iR_2$) is weaker than the same type of bond to a silyl group ($R'-SiR_3$).[24] Therefore the second Si-C bond in silacyclopropane breaks at an enthalpic cost of approximately $D(\dot{S}iH_2-CH_3) - D_\pi(H_2C{=}CH_2)$, where $D_\pi(H_2C{=}CH_2)$ is the π bond enthalpy in ethylene.[25]

Quantities such as $D(SiH_3-CH_3)$ are known much better than $D(\dot{S}iH_2-CH_3)$, so it would be advantageous to recast our expression in terms of the former. We might expect the SiH_3-CH_3 BDE to exceed that of $\dot{S}iH_2-CH_3$ by an amount which is roughly equal to the difference between the first and second BDE's of SiH_4. Walsh[11] has defined the latter difference to be the divalent state stabilization energy (DSSE) of SiH_2, i.e.

$$\mathrm{DSSE}(SiH_2) \equiv D(SiH_3{-}H) - D(\dot{S}iH_2{-}H) \qquad (3)$$

which allows us to express our approximation in the compact form

$$D(\dot{S}iH_2{-}CH_3) \cong D(SiH_3{-}CH_3) - \mathrm{DSSE}(SiH_2) \qquad (4)$$

In summary, the foregoing analysis leads to the following expression for the enthalpy change associated with the decomposition of silacyclopropane via reaction 1:

$$\Delta H(1) \cong 2D(SiH_3{-}CH_3) - \text{strain enthalpy} - D_\pi(H_2C{=}CH_2) - \mathrm{DSSE}(SiH_2) \qquad (5)$$

Table I. Divalent State Stabilization Energies (DSSE)[a] of Methylenes, Silylene, and Germylene

molecule	DSSE, kcal/mol	source(s) of data
CH_2 (triplet)	$-5._6$	refs 27 and 28
CH_2 (singlet)	$-14._6$	refs 27 and 28
CF_2 (singlet)	$45._4$	ref 23
SiH_2 (singlet)	$19._3$	ref 11
GeH_2 (singlet)	$25._8$	ref 29

[a] $\mathrm{DSSE}(MR_2) \equiv D(MR_3{-}R) - D(\dot{M}R_2{-}R)$.

Table II. π-Bond Enthalpies (D_π) in Group 14 Dimetallenes

bond	D_π, kcal/mol	source(s) of data
$H_2C{=}CH_2$	65	ref 30
$H_2C{=}SiH_2$	38	ref 30
$H_2C{=}GeH_2$	31	ref 31
$H_2Si{=}SiH_2$	25	refs 30 and 32
$H_2Si{=}GeH_2$	25	ref 32
$H_2Ge{=}GeH_2$	25	ref 32

Table III. $H_3M-M'H_3$ Bond Dissociation Enthalpies (kcal/mol) at 298 K

bond	$D(H_3M-M'H_3)$	source of data
H_3C-CH_3	$89._9$	ref 27
H_3C-SiH_3	$88._2$	ref 11
$H_3Si-SiH_3$	$73._6$	ref 11
H_3C-GeH_3	$78._2$	ref 29
$H_3Si-GeH_3$	70	estimated[a]
$H_3Ge-GeH_3$	$65._7$	ref 29

[a] Estimated to be the geometric mean of SiH_3-SiH_3 and GeH_3-GeH_3 bond dissociation enthalpies. This method of estimation is discussed in ref 26.

For the general case of the decomposition of c-$XH_2YH_2ZH_2$ to XH_2 and $H_2Y{=}ZH_2$ we obtain

$$\Delta H(1) \cong D(XH_3{-}YH_3) + D(XH_3{-}ZH_3) - \text{strain enthalpy} - D_\pi(H_2Y{=}ZH_2) - \mathrm{DSSE}(XH_2) \qquad (6)$$

Equations 5 and 6 show that what is missing from the thermochemical analysis discussed in the introduction is the DSSE term, which corrects one of the H_3X-M BDE's for the fact that the second bond being broken is actually a $H_2\dot{X}-M$ bond.

Results

The optimized geometries of the germanium-containing rings are of special interest and are shown in Figure 1. The rings containing only silicon and carbon have been studied numerous times,[5,6] and their geometries are not reproduced here. Qualitatively, the germanium rings exhibit the same structural features as silicon rings. Most noteworthy is digermirane, Ge_2CH_6, which has a very short Ge-Ge bond, 2.373 Å, and nearly planar bonding about the germanium centers, as in a π-complex. At the other extreme is germirane, which exhibits the opposite characteristics in the basal unit: long C-C distances and more highly pyramidalized bonding about the ethylene fragment. These trends are consistent with the notion that the primary determiner of the basal bond lengths in 3MRs is the electronegativity, or π-donating ability, of the apical substituent.[5b] One curious observation is that cyclotrigermane has bond distances that are longer than those in digermane, Ge_2H_6, at the same level of theory, 2.462 versus 2.457 Å. This is just the opposite of the case in cyclopropane and cyclotrisilane, where the bond distances in the rings are shorter than those in the straight-chain analogues.

Our thermochemical estimate of $\Delta H(1)$ using eq 6 employs a combination of experimental bond dissociation enthalpies (BDE's) and heats of formation and ab initio quantum mechanical data. DSSE and π-bond enthalpies used in evaluating $\Delta H(1)$ are shown in Tables I and II. The former are derived from experimental data, and the latter are theoretical rotation barriers in dimetallenes. In Table III we list selected values of $H_3M-M'H_3$ BDE's, all of which are experimental results at 298 K except the $H_3Si-GeH_3$ BDE. To our knowledge no reliable experimental or theoretical values of the $H_3Si-GeH_3$ BDE have been published, so we esti-

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[25] This is, effectively, the thermochemical π bond energy of Benson (reference 23), which defines $D_\pi(H_2M{=}M'H_2)$ as the difference between the BDE's of $MH_3M'H_2-H$ and $\dot{M}H_2M'H_2-H$ bonds. $D_\pi(H_2M{=}M'H_2)$ is also commonly defined as the double bond rotation barrier. These two definitions are not identical, but they have been found to yield very similar results where comparison can be made (see refs 30 and 31 for a comparison).

Table IV. Strain Enthalpies of Group 14 Cyclotrimetallanes

	strain enthalpy,[a] kcal mol^{-1}			
molecule	this research DZ+d SCF	this research DZ+d CCSD// DZ+d SCF	6-31G(d) SCF[b]	6-31G(d) MP2// 6-31G(d) SCF[b]
C_3H_6	26.1	28.1	25.9	27.3
SiC_2H_6	36.7	35.2	37.6	35.7
GeC_2H_6	38.1	35.8		
CSi_2H_6	39.7	37.0	41.2	38.6
Si_3H_6	36.8	34.5	37.5	35.6
$GeSi_2H_6$	37.8	35.6		
CGe_2H_6	41.7	39.2		
$SiGe_2H_6$	38.6	36.3		
Ge_3H_6	39.3	37.3		
$CSiGeH_6$	40.8	38.2		

[a] ΔH_0 for the homodesmotic reaction $YH_3XH_2ZH_3 + XH_3YH_2ZH_3 + XH_3ZH_2YH_3 \rightarrow c\text{-}XH_2YH_2ZH_2 + XH_3YH_3 + XH_3ZH_3 + YH_3ZH_3$. [b] Reference 6.

Table V. Energetics of the Decomposition Reactions $c\text{-}XH_2YH_2ZH_2 \rightarrow XH_2$ (singlet) + $H_2Y{=}ZH_2$

reaction	ΔE_{elec},[a] kcal mol^{-1}	ΔZPVE,[b] kcal mol^{-1}	ΔH, kcal mol^{-1} ab initio[a,c]	estimated[d]
$C_3H_6 \rightarrow CH_2 + C_2H_4$	93.2 (106.8)	−9.0	84.9 (98.6)	101
$SiC_2H_6 \rightarrow SiH_2 + C_2H_4$	38.1 (47.5)	−4.7	33.9 (43.2)	57
$GeC_2H_6 \rightarrow GeH_2 + C_2H_4$	13.1 (22.0)	−4.1	9.3 (18.3)	30
$CSi_2H_6 \rightarrow SiH_2 + CSiH_4$	60.8 (64.7)	−4.9	56.4 (60.3)	$67._5$
$Si_3H_6 \rightarrow SiH_2 + Si_2H_4$	63.0 (66.6)	−4.8	58.7 (62.3)	68
$GeSi_2H_6 \rightarrow GeH_2 + Si_2H_4$	55.3 (56.4)	−4.3	51.4 (52.5)	54
$CGe_2H_6 \rightarrow GeH_2 + CGeH_4$	47.2 (48.4)	−4.3	43.3 (44.5)	48
$SiGe_2H_6 \rightarrow GeH_2 + SiGeH_4$	53.4 (53.4)	−4.1	49.7 (49.7)	49
$Ge_3H_6 \rightarrow GeH_2 + Ge_2H_4$	51.1 (50.7)	−4.0	47.5 (47.1)	43
$CSiGeH_6 \rightarrow GeH_2 + CSiH_4$	44.1 (46.9)	−4.4	40.2 (42.9)	46
$SiC_2H_6 \rightarrow CH_2 + CSiH_4$	109.3 (120.5)	−8.4	101.6 (112.8)	$119._5$
$GeC_2H_6 \rightarrow CH_2 + CGeH_4$	104.5 (114.8)	−8.3	96.9 (107.3)	116
$CSi_2H_6 \rightarrow CH_2 + Si_2H_4$	116.5 (127.2)	−7.6	109.5 (120.3)	129
$GeSi_2H_6 \rightarrow SiH_2 + SiGeH_4$	62.9 (63.9)	−4.5	58.8 (59.8)	64
$CGe_2H_6 \rightarrow CH_2 + Ge_2H_4$	97.4 (106.5)	−7.1	91.0 (100.1)	107
$SiGe_2H_6 \rightarrow SiH_2 + Ge_2H_4$	60.7 (61.4)	−4.4	56.7 (57.3)	59
$CSiGeH_6 \rightarrow SiH_2 + CGeH_4$	64.3 (66.7)	−4.8	59.9 (62.3)	70
$CSiGeH_6 \rightarrow CH_2 + SiGeH_4$	107.3 (116.8)	−7.2	110.7 (110.2)	118

[a] Values not in parentheses are DZ+d SCF results. DZ+d CCSD//DZ+d SCF data are enclosed in parentheses. [b] Zero-point harmonic vibrational energies determined at the DZ+d SCF level of theory. [c] ΔH_0(ab initio) = ΔE_{elec} + (0.91)(ΔZPVE). [d] Estimated using eq 6, as discussed in the text.

mated this value to be the geometric mean of the $H_3Si{-}SiH_3$ and $H_3Ge{-}GeH_3$ BDE's.[26] Strain enthalpies, assumed to be equal to ΔH of reaction 2, were computed by the ab initio methods discussed earlier. The theoretical thermodynamic data (π-bond and strain enthalpies) are 0 K values.

Our computed ring strain enthalpies are shown in Table IV along with previous theoretical results of Boatz and Gordon.[6] Electron correlation has only a small (2–3 kcal mol^{-1}) effect upon the strain enthalpies, as is expected for homodesmotic reactions,[22] so it is not surprising that the computed strain enthalpy of cyclopropane is close to the value of $\Delta H_{298}(2)$ = 26.5 kcal mol^{-1} obtained from experimental heats of formation.[33] Boatz and Gordon obtained similar results using a 6-31G(d) basis set, which is comparable to our DZ+d set. The strain energy of cyclotrigermane obtained in this study, 37.3 kcal mol^{-1}, is notably smaller than the 44.6 kcal mol^{-1} value found by Nagase and Nakano[5e] using smaller basis sets and SCF energies. In the analysis that follows, only the CCSD strain enthalpies were used to estimate $\Delta H(1)$.

Values of the theoretically obtained enthalpy for the decomposition of each 3-membered ring into a singlet divalent species $:XH_2$ and a doubly bonded compound $H_2Y{=}ZH_2$ (reaction 1) are listed in Table V, along with the predictions obtained using eq 6 and the data in Tables I–IV. The first ten entries in Table V correspond to the most stable products, and these are followed by the remaining eight possible decomposition pathways. Cyclopropane is the only system for which sufficient experimental data are available for comparison, and in that case the CCSD prediction of $\Delta H_0(1)$ = 98.6 kcal mol^{-1} agrees very well with the value of 99.4 kcal mol^{-1} obtained from 0 K experimental heats of formation.[28,34] This agreement is not unexpected, because for isogyric[35] reactions (of which reaction 1 is an example) correlated ab initio methods usually yield reaction energies which are accurate to within a few kcal mol^{-1} if polarized basis sets are used.

The estimated cyclotrimetallane decomposition enthalpies (from eq 6) and the CCSD theoretical results differ by fewer than 10 kcal mol^{-1} in all but two cases, silirane and germirane, for which we observe discrepancies of about 14 and 12 kcal mol^{-1}, respectively. In light of the approximations inherent in eq 6 and the imprecision of the experimental and theoretical data, we judge this to be rather good agreement. On the other hand, the errors

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appear to be systematic; 16 of the 18 estimated values exceed the corresponding CCSD predictions. But even if the theoretical and experimental data were perfectly accurate and eq 6 contained no approximations, each estimated value of $\Delta H(1)$ would exceed the corresponding CCSD prediction by a few kcal mol^{-1}, because the latter are valid for a temperature of 0 K while the former were evaluated using a mixture of 298 and 0 K data. Translational and rotational terms contribute $8RT$, or 4.7 kcal mol^{-1}, to values of $\Delta H(1)$ estimated using 298 K BDE's and 0 K strain enthlapies.

One might begin to refine our thermochemical analysis of cyclotrimetallane decomposition by attempting to include the effect of the third ring atom upon the BDE of the other two. For example, one might replace $2D(SiH_3\text{–}CH_3)$ in eq 5 by $D(CH_3\text{-}SiH_2\text{–}CH_2CH_3) + D(SiH_3\text{–}CH_2CH_3)$. It would also be possible to replace eq 4 with a slightly better approximation for $D(\dot{S}iH_2\text{–}CH_3)$. However, the cumulative effect of these refinements would probably amount to no more than about 10 kcal mol^{-1}, would not change the trends in $\Delta H(1)$ values, and thus would not give much additional insight into the thermochemistry of cyclotrimetallane decomposition. We believe that more elaborate approximation schemes are not justified at this time given the uncertainties in the experimental BDE's and theoretical data.

Analysis and Discussion

It is interesting that all the 3-membered rings studied here have CCSD strain enthalpies which are clustered within a 5 kcal mol^{-1} range with the exception of cyclopropane, whose strain enthalpy lies 6 kcal mol^{-1} below this range (Table IV). Boatz, Gordon, and Hilderbrandt[36] have interpreted the strain enthalpies of 3-, 4-, 5-, and 6-membered cycloalkane and monosilacycloalkane rings in terms of a simple group additivity model and found that for any given ring bond angle near 60° a $>SiH_2$ group is significantly more strained than a $>CH_2$ group. Our results are not inconsistent with this interpretation and also indicate that $>SiH_2$ and $>GeH_2$ groups are about equally strained at 60°.

Because $\Delta S(1)$ should not differ greatly among the 10 cyclotrimetallanes considered here, the relative stabilities of these compounds with respect to dissociation to a carbene-like species and a dimetallene will be determined primarily by $\Delta H(1)$. Therefore, cyclopropane is predicted to be significantly more stable than the other 3-membered rings, consistent with experimental observations, and by far the least endothermic decomposition belongs to the elusive germirane! Silirane and the remaining germanium-containing rings are more susceptible to thermolysis than CSi_2H_6 or Si_3H_6. Equation 6 readily provides explanations of these trends. Contributing to the instability of GeC_2H_6 relative to C_3H_6 is the former's larger ring strain, the weakness of C–Ge bonds compared to C–C bonds, and a more stable XH_2 decomposition product (manifested in a large positive DSSE for GeH_2 vs a negative DSSE for CH_2). Strong C–C single bonds, low strain, and relatively unstable CH_2 make C_3H_6 the most stable cyclotrimetallane in spite of the extremely strong C–C π-bond. The importance of the DSSE in the thermochemistry of group 14 divalent species is not always appreciated. In fact, the 34 kcal mol^{-1} difference in the DSSE's of singlet CH_2 and SiH_2 accounts for *most* of the difference in the enthalpies of the cyclopropane and silirane decomposition reactions!

The disparate behavior of carbenes, silylenes, and germylenes in their addition to 1,3 dienes is conveniently explained by a comparison of the enthalpies of decomposition of the cyclopropane, silirane, and germirane rings. Although the first step in the reaction of singlet carbenes and silylenes with 1,3 dienes is typically 1,2 cycloaddition,[7,37] germylene reactions yield products consistent with stereospecific, disrotatory 1,4 cycloaddition.[38] Thus, the germylene addition is either concerted[38] or occurs via an extremely short-lived germirane intermediate,[9d] consistent with the comparative instability of germirane relative to cyclopropane and silirane. Like germylenes, stannylenes also react with 1,3 dienes to yield products consistent with stereospecific, disrotatory 1,4 cycloaddition and have never been observed to add to isolated C=C bonds.[38] These observations make thermochemical sense; the stannirane ring ($c\text{-}SnH_2CH_2CH_2$) might be expected to be even less stable than germirane because Sn–C bonds are weaker than Ge–C bonds.[39] Plumbirane is almost certainly thermodynamically unstable with respect to dissociation into ethylene and PbH_2.

Although the effects of ring substituents upon the enthalpy of ring decomposition have not been studied extensively, these can be estimated from our thermochemical analysis because substituent effects upon BDE's, DSSE's, ring strain, and π-bond enthalpies are known to some extent. This permits us to rationalize the contrasting behaviors of cyclopropane and hexafluorocyclopropane upon heating, for example. Hexafluorocyclopropane is apparently far less stable than cyclopropane with respect to decomposition via reaction 1, because although the former decomposes to difluorocarbene and tetrafluoroethylene at 160 °C,[8] the latter can be heated to 400 °C before it isomerizes to propene.[40] The reasons for this are clear: not only is the DSSE of CF_2 roughly 60 kcal mol^{-1} more positive than that of singlet methylene (see Table I), perfluorination also increases the ring strain of cyclopropane by at least 20 kcal mol^{-1}.[41] These ring-destabilizing effects are only partially moderated by the concomitant weakening of the ethylene π-bond[42] and strengthening of the C–C single bonds[23] by about 10 kcal mol^{-1} each upon perfluorination. Therefore, the decomposition of hexafluorocyclopropane is predicted to be less endothermic than that of cyclopropane by a whopping 50–60 kcal mol^{-1}, which is in qualitative agreement with the experimental observations, and a prediction of $\Delta H(1)$ of 36 kcal mol^{-1} from published heats of formation for $c\text{-}C_3F_6$, C_2F_4, and CF_2.[34,43] It also makes sense that tetrafluorocyclopropane undergoes thermolysis less readily than hexafluorocyclopropane.[8]

The substituents to the ring can have other interesting effects. For example, the proper choice of substituents can entirely reverse the relative stability of cyclopropane rings relative to disilacyclopropane rings, and even alter the preferred mode of decomposition. Consider the case of cyclopropanone versus disilacyclopropanone, where we have substituted a C=O group for CH_2 in the parent rings. The C=O group is known[44] to have a huge DSSE of about 73 kcal mol^{-1}. Considering only the relative effects of DSSE on the reaction enthalpy, this suggests that the decomposition of cyclopropanone to carbon monoxide and ethylene is endothermic by about 14 kcal/mol. On the other hand, the disilacyclopropanone decomposition would now take place via extrusion of carbon monoxide, not a silylene as in the parent compound, and would require more energy, about 38 kcal mol^{-1}, than does cyclopropanone, mainly because of the stronger C=C π-bond. Silylene extrusion to form a silaketene would likely require nearly 30 kcal/mol more energy than CO extrusion, because the larger DSSE of CO overwhelms small differences in Si=C versus Si=Si π-bond strengths. Considering an almost certain, probably substantial, increase in strain in these rings due to the presence of an sp^2-hybridized ring atom, these estimates are all probably too high by 20 kcal mol^{-1} or more. A similar result is obtained in an analysis of cyclopropanimines relative to disilacyclopropanimines,[45] because the parent isonitrile HN=C also has a large DSSE[44] of about 78 kcal mol^{-1}. That is, disilacyclopropanimines will preferentially extrude HN=C instead of SiH_2 and will be more thermodynamically stable than cyclo-

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propanimines with regard to this process.

One can also imagine replacing CH_2, SiH_2, and GeH_2 ring atoms by other groups. This would necessitate only minor changes in our working equation, eq 6. One group of possible replacements worth mentioning is the heavier chalcogens, selenium and telurium. In the last few years, stable M_2Se and M_2Te rings have been synthesized for M = Si, Ge, and Sn.[46] On the other hand, C_2Se rings are unstable, and C_2Te rings have apparently never been made. The origin of the relative stability for the Si, Ge, and Sn rings can be traced to the much weaker π-bonds. In the case of C_2Se and C_2Te rings, the strong π-bond in ethylene provides a significant thermochemical driving force for extrusion of a selenium or telurium atom. In Si, Ge, and Sn rings, this driving force is severely attenuated.

Baines and co-workers[4b] have just reported a fascinating consequence of what our results suggest is a small enthalpy difference in cyclotrimetallane decomposition enthalpies. With the ultimate goal of obtaining a Ge═Si doubly bonded compound, it was decided that the best choice of precursor was a siladigermirane, which it was hoped would decompose according to eq 1 to give the desired germasilene product.[32] Unfortunately, and for unknown reasons, the synthetic route also produced some cyclotrigermane, which could not be separated from the desired precursor by traditional means. It was found, however, that the cyclotrigermane was more thermally labile than the siladigermirane, and the minor component Ge_3 ring was eliminated from the mixture by thermolysis at a reduced temperature. According to our results in Table V for the parent hydride compounds, the cyclotrigermane decomposition has a endothermicity of 47.1 kcal mol^{-1} compared to siladigermirane's 49.7 kcal mol^{-1}. If we assume that the reverse of reaction 1 occurs without barrier so that the endothermicity can be equated with the activation energy, this corresponds to a factor of 40 in the individual rate constants for decomposition at the temperature employed, 80 °C.

Concerning the prospects for synthesizing new cyclotrimetallane rings, we note that the decompositions of $GeSi_2H_6$ and $CSiGeH_6$ are no less endothermic than the decompositions of other rings which have already been synthesized (albeit in highly substituted form), suggesting that $GeSi_2$ and CSiGe rings may be accessible by established synthetic routes. On the other hand, the germirane ring, whose decomposition is ca. 20 kcal mol^{-1} less endothermic than those of any of the other cyclotrimetallanes, clearly presents a greater challenge, and stannirane rings will likely prove even more difficult (vide ante). But if the cyclopropane ring can be destabilized by perfluorination then it ought to be possible to stabilize the germirane ring through judicious substitution for the hydrogen atoms. Replacing the H atoms on Ge with electropositive π-acceptor substituents such as SiH_3 may stabilize the germirane ring by reducing both the ring strain[47] and the DSSE of Ge,[44] although these effects will probably be mitigated by weakening of the Ge–C bonds.[48] Reductions in the C–C π-bond enthalpy (assuming it can be equated with the double bond rotation barrier[25]) of over 20 kcal mol^{-1} can be achieved by placing "push-pull" substituents on the C atoms,[49] and it may be possible to find a pair of these substituents which produce a low C–C π-bond enthalpy without adversely affecting the other contributions to the enthalpy of reaction 1. Thus, the use of carefully chosen substituents is probably the key to the synthesis of germirane and the stabilization of other cyclotrimetallane rings.

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^{27}Al Nuclear Magnetic Resonance Study of Aluminas and Their Surfaces

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Abstract: The nature of the surface of α-, γ-, and transition-aluminas has been explored via variable-temperature solid-state ^{27}Al NMR spectroscopy. Results from a previous study of aluminas using ^{27}Al NMR at room temperature showed a loss in signal with increasing surface area. The conclusion based upon these results was that the aluminum atoms in the first two molecular layers of alumina did not contribute to the ^{27}Al NMR signal. Further, the observed signal loss was due to the surface aluminum atoms experiencing a large electric field gradient. Results from the study presented here indicate that a loss in ^{27}Al signal with increasing surface area is real but that it is due instead to dynamic events occurring at the surface. Low-temperature studies served to slow these dynamics, thereby increasing the observable signal by amount greater than expected from the Boltzmann factor alone. We present these data herein and propose mechanisms by which these surface dynamics may occur.

Introduction

Aluminas, general formula Al_2O_3, have been known to have catalytic importance since the late 1700s. Either by themselves, or as supports, the aluminas are responsible for a wide range of catalytic reactions, and the properties of aluminas have been the subject of many investigations.[1] The major emphasis on aluminas today is in their role as supports for metals, mixed-metal oxides, and metal oxides in industrial catalytic processes. The aluminas of choice for these systems are often η- and γ-alumina, with typical respective surface areas of 250 and 220 m^2/g. The surface structure of these and other transition-aluminas is the key to more educated proposals for mechanisms of reactions over these catalytic systems.

What is known about the surface structure of these catalyst supports has resulted from IR studies on surface hydroxyl groups,[2,3]

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