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Relative Stability of Multiple Bonds to Silicon: An ab Initio Study of C_2SiH_4 Isomers

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Abstract: Ab initio (6-31G*//3-21G) SCF calculations have been carried out on 15 isomers with the chemical formula C_2SiH_4. The isomers include structures with formal double and triple bonds to silicon, as well as carbenes and silylenes, so a direct comparison of these types of species is possible. The isomerization energies provide an opportunity to consider the relative strengths of analogous bonds to carbon and silicon. With the appropriate isodesmic reactions, the stabilizing or destabilizing effects of substituents and strain in three-membered rings both may be investigated.

I. Introduction

During the past several years, there has been a steadily increasing interest among quantum chemists in molecules containing silicon. Much of this interest has centered around the nature of the elusive silicon–carbon double bond[1] or its silylene isomer.[1a,2] More recently, attention has expanded to silicon–silicon double bonds,[3] triple bonds containing silicon,[4-8] and strain in small silicon-containing rings.[9] This increasing body of knowledge has helped to elucidate the nature of bonding in silicon compounds, particularly those containing multiple bonds to silicon.

It is often the case that differentiation between alternative sets of products in a thermochemical or photochemical reaction rests on *relative* bond energies (BE) in the molecules of interest. For example, it may well be as useful to know the relative values for the bond energy differences [BE(C=C) - BE(C—H)] vs. [BE(C=Si) - BE(Si—H)] as it is to know BE(C=C) or BE(C=Si) individually. From a theoretical point of view, a comparison of bond energy differences is more accessible than individual bond energies since one might expect a less critical dependence on correlation error in the former case. This speculation is supported by the success[10] at the Hartree–Fock level of predicting the relative energies of isomers, such as propyne, allene, and cyclopropene, which contain rather different bond types.

In order to gain some insight into the bonding of silicon, particulary in relation to the behavior of carbon in similar chemical environments, a systematic study of a series of compounds which contains a wide variety of bonding situations is required. The simplest such series is the set of 15 structural isomers with the empirical formula C_2SiH_4. Represented within these isomers are single, double, and triple bonds involving silicon, strained rings, and cyclic and acyclic carbenes and silylenes. Thus, these 15 isomers collectively provide the focus of the present work. Additional molecules, such as the products of bond separation reactions[11] or those needed to evaluate ring strain,[12] have been included as needed.

Table I. Relative Isomer Energies (kcal/mol)

isomer	BTB[a]	6-31G*// 3-21G	3-21G// 3-21G
1	0.0	0.0	0.0
2		13.36	3.61
3	16.99	14.68	1.24
4	16.63	14.79	22.11
5		15.89	2.60
6		28.88	26.91
7		35.39	39.17
8	45.73	50.11	39.28
9	60.74	61.92	47.54
10		65.22	62.53
11		66.30	56.00
12		75.44	78.74
13		84.30	87.68
14		90.70	87.75
15		90.80	85.82

[a] Reference 5.

Some of the 15 isomers have been the subject of previous theoretical treatments.[5,9] Of these, the most comprehensive study has been that by Barthelat, Trinquier, and Bertrand.[5] These authors used a pseudopotential method with a double-ζ basis set to investigate five of the isomers to be considered here, including 3-sila-1-propyne, the only isomer whose structure has been determined experimentally.[13]

Following a summary in section II of the methodology used in this work, the results of the structural determinations and the associated energetics and electron density distributions are discussed in section III. The implications of these results with regard to bonding in silicon are discussed in section IV.

II. Methodology

All geometry optimizations were carried out by using the split valence 3-21G basis set[14] and the analytical gradient scheme contained within the HONDO system of programs.[15] To obtain more reliable values for relative energies and electron densities, single-point calculations were performed at the 3-12G geometries

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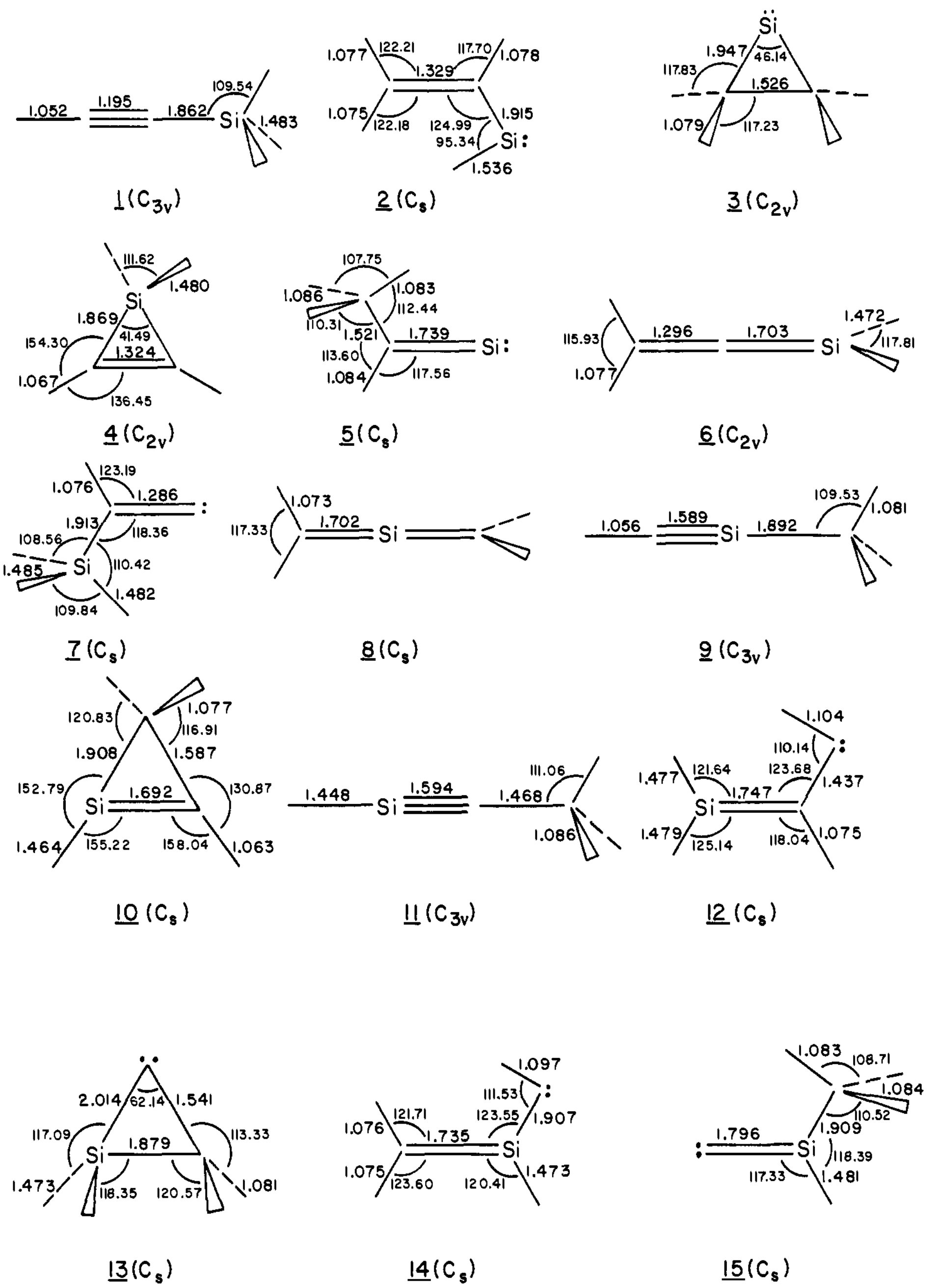

1 (C_{3v}) 2 (C_s) 3 (C_{2v})

4 (C_{2v}) 5 (C_s) 6 (C_{2v})

7 (C_s) 8 (C_s) 9 (C_{3v})

10 (C_s) 11 (C_{3v}) 12 (C_s)

13 (C_s) 14 (C_s) 15 (C_s)

Figure 1. Molecular structures. Bond lengths are given in Å and angles in deg. The assumed symmetry is given in parentheses.

by using the extended 6-31G* basis set.[10,16] Such single-point calculations are denoted 6-31G*//3-21G.[14] All calculations have been restricted to the closed shell singlets.

In addition to a straightforward comparison of relative isomer energies, use will be made of the concept of bond-separation reactions introduced by Pople and co-workers.[11] In such a reaction, the molecule of interest is reduced to the simplest set of two-heavy-atom prototypes which contain the original bond types. For example, the reaction for propene is

$$CH_3—CH{=}CH_2 + CH_4 \rightarrow CH_3—CH_3 + CH_2{=}CH_2 \quad (I)$$

In bond-separation reactions the number of bonds of each type is qualitatively conserved (i.e., they are *isodesmic*) so that the correlation contribution to the computed ΔE's is expected to be minimal. Thus, these reactions, which provide some estimate of the stabilization or destabilization of the parent relative to isolated bond types, are well represented within the Hartree–Fock approximation.[11]

III. Results

The calculated structures for the 15 isomers are displayed in Figure 1, and the corresponding relative energies are listed in Table I. For comparison, the 3-21G structures[14] for the simplest prototype molecule for each type of bond are shown in Figure 2. The predicted geometry for 3-sila-1-propyne (**1**) is in good agreement with both the experimental[13] and previous theoretical[5] results. As one would expect as a result of π delocalization, the C≡C triple bond is somewhat longer and the Si–C bond somewhat shorter than the corresponding isolated bonds. Similar behavior is found for the related structures **9** and **11** and in the structures containing "classical" double bonds (**2**, **12**, and **13**). The double bonds in both silaallenes (**6** and **8**) are shorter than their isolated counterparts.

In silylenes C–Si bonds appear to be longer than their "normal" counterparts. While structure **2** (vinylsilylene) appears to be an exception to this observation, there is undoubtedly a shortening due to the adjacent double bond. Thus, the corresponding bond in vinylsilane is 0.02 Å shorter.[9] In contrast, the carbene structures do not follow this pattern. The C–Si bond lengths in **14** and **15**,

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(16) M. S. Gordon, *Chem. Phys. Lett.*, **76**, 163 (1980).

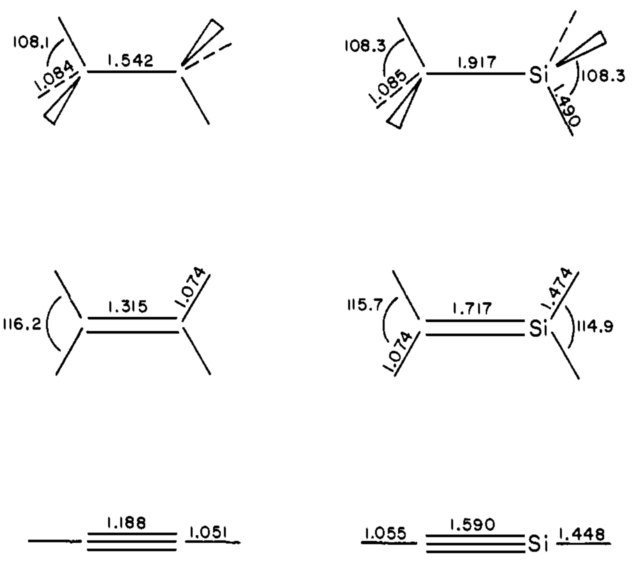

Figure 2. Molecular structure for prototypes.

for example, are shorter than those in methylsilylene and silaethylene, respectively.

Where comparisons are possible, the relative energies predicted by Barthelat et al.[5] are in good agreement with those predicted by 6-31G* (Table I). On the other hand there are some large differences between the 6-31G* and 3-21G results. Since the pseudopotential basis set[5] included d orbitals on silicon but not on carbon, it appears that the latter are not critical for the prediction of the relative energies investigated here.

Some general comments may be made based on the results presented in Table I. Aside from **1**, the three silylenes are among the most stable isomers. In contrast, the carbenes are generally found to be rather unstable. An apparent exception to this is structure **7**; however, here one has also obtained a saturated silyl group, apparently a relatively stable moiety. It has been noted previously[16] that for a given carbon–silicon bond, methyl substitution appears to be preferred at the silicon end rather than at the carbon end. This is apparently related to an unfavorable increase in electron density at the silicon when substitution occurs at the carbon. This trend is apparent in the C≡Si triple bond (structures **9** and **11**). The calculated atomic charges in Figure 3 support the above interpretation since the silicon is actually slightly negative in **11**. A similar result is found for the C–Si single bond in methylsilane (see section IV). On the other hand, carbene substitution on the C=Si bond in silaethylene occurs preferentially at the carbon end. The correlation with the electron density on silicon holds up here since silicon is rather more positive in **12** than in **14**. That this relationship between stability and the positive charge on silicon should not be taken too far may be seen by comparing the two silaallenes, structures **6** and **8**. The more stable structure, 1-silaallene, is more than 20 kcal/mol lower in energy and yet has a considerably smaller positive charge.

Recent calculations[8] have indicated that silylidenes are considerably more stable than the corresponding silaethynes. The 6-31G* energy difference between silaethyne and silylidene is approximately 56 kcal/mol. A comparison of **5** with **9** and **11** indicates that methyl substitution has a small stabilizing effect on the carbon–silicon triple bond but that the silylidene is still much more stable. On the other hand, silyl vinylidene (**7**) is much higher in energy than 3-silyl-1-propyne. Again, this is consistent with the relative energies in the unsubstituted species.[17]

IV. Discussion

A. Bond-Separation Reactions. The bond-separation reactions which break each of the 15 isomers into their simplest prototypes are listed in Table II. Since each reaction is characterized by a formal conservation of bond type, a zero-energy difference would correspond to complete transferability of bond energies. An exothermic (endothermic) reaction indicates that the parent molecule has been destabilized (stabilized) relative to the separated bonds. Note that the reactions in Table II are listed in order of decreasing stability of the parent molecule.

Table II. Bond Separation Reactions

	reaction	ΔE,[b] kcal/mol
(1)	$HC{\equiv}C{-}SiH_3 + CH_4 \rightarrow HC{\equiv}CH + CH_3{-}SiH_3$	12.43
(2)	$H_2C{=}CH{-}\ddot{Si}H + CH_4 \rightarrow H_2C{=}CH_2 + CH_3{-}\ddot{Si}H$	7.03
(3)	$3^a + \ddot{Si}H_2 + 2CH_4 \rightarrow 2CH_3{-}\ddot{Si}H + CH_3{-}CH_3$	−23.42
(4)	$4^a + SiH_4 + 2CH_4 \rightarrow 2SiH_3{-}CH_3 + H_2C{=}CH_2$	−43.38
(5)	$CH_3CH{=}Si{:} + CH_4 \rightarrow CH_3{-}CH_3 + H_2C{=}Si{:}$	0.14
(6)	$H_2C{=}C{=}SiH_2 + CH_4 \rightarrow H_2C{=}CH_2 + H_2C{=}SiH$	−3.12
(7)	$H_3SiCH{=}C{:} + CH_4 \rightarrow H_3Si{-}CH_3 + H_2C{=}C{:}$	11.18
(8)	$H_2C{=}Si{=}CH_2 + SiH_4 \rightarrow 2H_2C{=}SiH_2$	−8.60
(9)	$HC{\equiv}Si{-}CH_3 + SiH_4 \rightarrow HC{\equiv}SiH + H_3Si{-}CH_3$	2.09
(10)	$10^a + SiH_4 + 2CH_4 \rightarrow CH_3{-}CH_3 + CH_3{-}SiH_3 + CH_2{=}SiH_2$	−69.82
(11)	$HSi{\equiv}C{-}CH_3 + CH_4 \rightarrow HSi{\equiv}CH + CH_3{-}CH_3$	5.97
(12)	$H_2Si{=}CH{-}\ddot{C}H + CH_4 \rightarrow H_2Si{=}CH_2 + CH_3{-}\ddot{C}H$	19.44
(13)	$13^a + \ddot{C}H_2 + CH_4 + SiH_4 \rightarrow SiH_3{-}\ddot{C}H + CH_3{-}\ddot{C}H + SiH_3{-}CH_3$	−44.47
(14)	$H_2C{=}SiH{-}\ddot{C}H + SiH_4 \rightarrow H_2C{=}SiH_2 + H_3Si{-}\ddot{C}H$	5.23
(15)	${:}C{=}SiH{-}CH_3 + SiH_4 \rightarrow {:}C{=}SiH_2 + H_3Si{-}CH_3$	0.98

[a] Number refers to number of isomer in Figure 1. [b] All energies are obtained from 6-31G*//3-21G calculations except for the molecules CH_3SiH_3, $H_2C{=}C$, SiH_3CH, and CH_3SiH. The latter are obtained from 6-31G*//4-31G calculations.

The most strikingly exothermic reactions are those involving the cyclic molecules—reactions 3, 4, 10, and 13 in Table II. This is one indication that the rings are strained, so that the bonds in the rings are weakened relative to their isolated counterparts. According to these reactions the cyclic silylenes and carbenes are relatively less strained than their formally unsaturated counterparts. An alternative approach to ring strain is to consider the conversion of the strained ring into molecules which contain the same groups in an unstrained environment.[12] For silacyclopropylidene (**3**), the appropriate isodesmic reaction is

$$3 + 3C_2H_6 \rightarrow (CH_3)_2\ddot{Si} + 2(CH_3)_2CH_2 \qquad \text{(II)}$$

The calculated (6-31G*//3-21G) ΔE for this reaction is −26.5 kcal/mol. In comparison, the ring strain in silacyclopropene has previously been calculated to be about −49 kcal/mol. Again, this is an indication that strain is relieved to some extent in the silylene relative to the unstrained systems. It is tempting to ascribe this relief to the larger apex angle in silacyclopropylidene; however, note that in silacyclopropane, for which the calculated ring strain is twice that of silacyclopropylidene,[9] the apex angle is 2° larger. At the same time, the C–C bond length in the cyclic silylene is rather short (cf. Figure 2), and this should have a stabilizing effect.

The bond-separation reactions for both silaallenes are exothermic, an indication that placing double bonds adjacent to each other has a destabilizing effect. Apparently, the effect is greater for two Si=C double bonds than for adjacent C=C and C=Si double bonds. The corresponding bond-separation energy for allene is −4.4 kcal/mol. It is interesting to note that the double bond lengths in both allenes are actually shorter than those in ethylene and silaethylene; thus, a simple bond length–bond energy relationship does not apply here.

The endothermicity of reaction 1 indicates a stabilization relative to the isolated bonds. Comparison of the geometries in Figures 1 and 2 indicates that the stabilization is apparently due to a trade-off between the slight weakening of the triple bond and the strong stabilization of the C–Si bond due to delocalization.

Among the remaining endothermic bond separation reactions, the most prevalent types of parent compound are silylenes and carbenes. The most endothermic of all is 1-silavinyl-2-carbene (**12**) with a ΔE of 19.4 kcal/mol. Comparison of Figures 1 and

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(17) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem.*, **14**, 545 (1978).

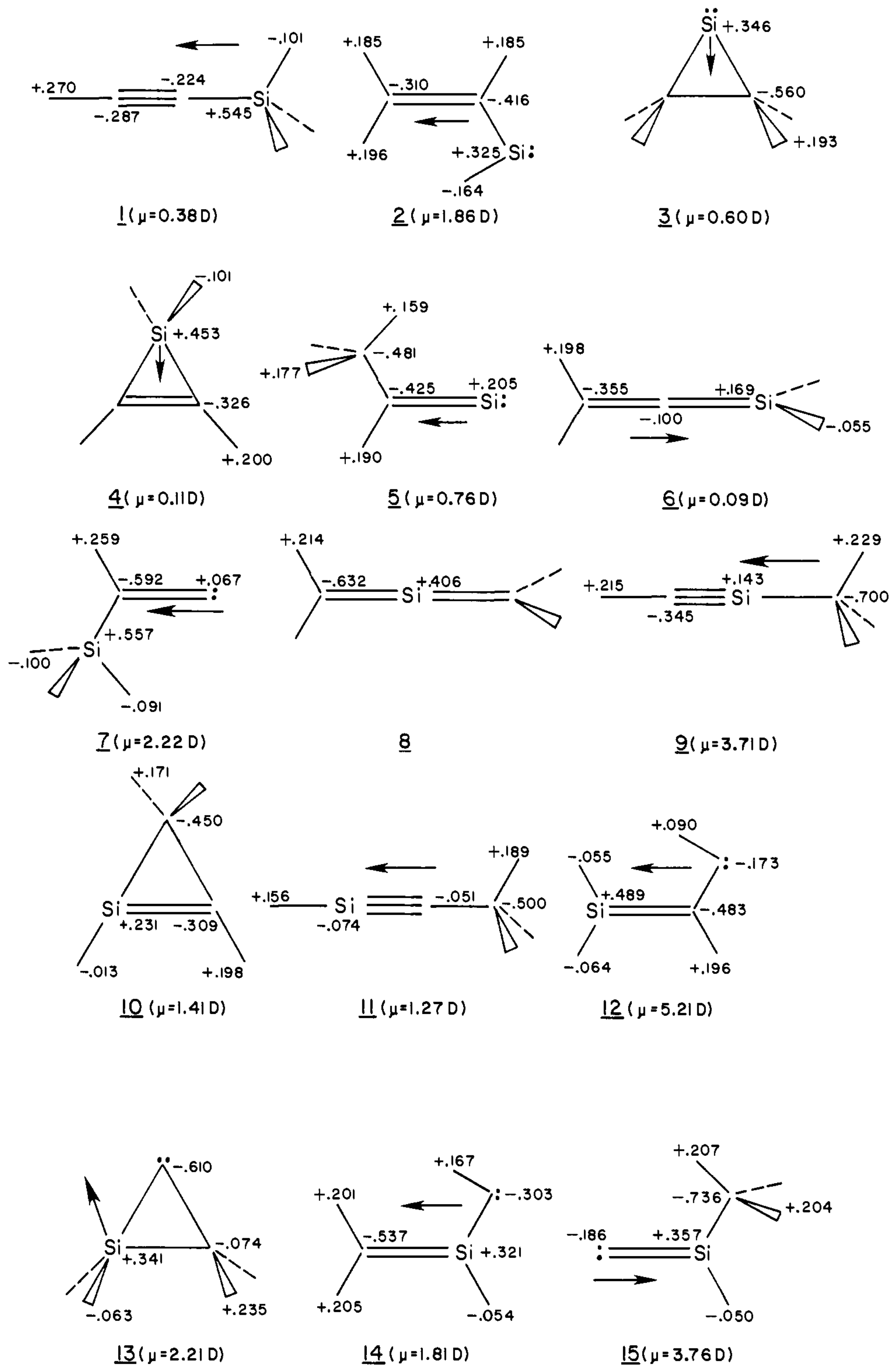

Figure 3. Net atomic charges. The dipole moments are given in parentheses, and the arrows indicate the approximate direction of the dipole moments.

2 indicates that the Si=C bond has been lengthened by 0.03 Å as a result of substitution. At the same time, the C–C: bond has been shortened by 0.075 Å relative to ethylidene,[18] presumably due to the π-delocalization effect, and this apparently has a strong stabilizing effect. Similar comments apply to vinylsilylene (R-($\ddot{\mathrm{Si}}$–C) in methyl silylene is 0.05 Å longer) and to 1-silavinyl-1-carbene (R(Si–$\ddot{\mathrm{C}}$) in silyl carbene is 0.05 Å longer). The bond-separation reaction for silylvinylidene is also strongly endothermic, but here the geometric effect is a slight shortening of both the C=C: (0.01 Å) and C–Si (0.004 Å) bonds. The net C=C overlap population is 0.653 in silylvinylidene and 0.611 in vinylidene; however, the pπ–pπ overlap population is actually larger in vinylidene. The pπ–dπ overlap population is an order of magnitude smaller than pπ–pπ and about the same for the two molecules. Thus, the stabilization of the C=C bond is apparently a σ effect.

The two isomers containing a C≡Si triple bond (**9** and **11**) are also stabilized by methyl substitution. In both isomers, only slight changes occur in the C≡Si bond length. On the other hand, the Si–C bond in **9** and the C–C bond in **11** become shorter by 0.025 Å and 0.074 Å, respectively.

B. Carbenes and Silylenes. The 15 isomers provide an opportunity to examine 1,2-hydrogen shifts between carbenes or silylenes and the corresponding doubly or triply bonded species. The energy changes resulting from 13 such reactions are listed

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(18) M. S. Gordon, unpublished results.

(19) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.*, **10**, 1 (1976).

Table III. Isomerizatons of Silylenes and Carbenes

	reaction	ΔE,[b] kcal/mol
(1)	$\mathrm{CH_3\ddot{S}iH \rightarrow CH_2{=}SiH_2}$[a]	5.2 (−2.1)
(2)	$\mathrm{(CH_3)_2\ddot{S}i \rightarrow CH_3SiH{=}CH_2}$[a]	5.1
(3)	$\mathrm{CH_3CH_2\ddot{S}iH \rightarrow CH_3CH{=}SiH_2}$[a]	4.4
(4)	$\mathrm{H_2C{=}CH{-}\ddot{S}iH \rightarrow H_2C{=}C{=}SiH_2}$	15.5
(5)	$3 \rightarrow 10$[c]	50.5
(6)	$\mathrm{CH_3CH{=}\ddot{S}i \rightarrow CH_3C{=}SiH}$	50.4
(7)	$\mathrm{CH_3\ddot{C}H \rightarrow CH_2{=}CH_2}$	−69.1 (−83.6)
(8)	$\mathrm{SiH_3\ddot{C}H \rightarrow SiH_2{=}CH_2}$	−54.4
(9)	$\mathrm{SiH_3CH{=}\ddot{C} \rightarrow SiH_3C{\equiv}CH}$	−35.4
(10)	$\mathrm{SiH_2{=}CH{-}\ddot{C}H \rightarrow H_2Si{=}C{=}CH_2}$	−46.6
(11)	$\mathrm{CH_2{=}SiH{-}\ddot{C}H \rightarrow H_2C{=}Si{=}CH_2}$	−40.6
(12)	$13 \rightarrow 4$[c]	−69.5
(13)	$13 \rightarrow 10$[c]	−19.1

[a] From ref 16. [b] Values in parentheses are 6-31G* calculations augmented by second-order perturbation (MP2) corrections. [c] Numbers refer to isomers in Figure 1.

in Table III. Reaction 1 in Table III is the basic silylene to silaethylene isomerization, and the next two reactions indicate that methyl substitution at either end of the C–Si bond has little effect. While the SCF results indicate that the silylenes are more stable, addition of second-order perturbation corrections (MP2)[19] in the simplest reaction places silaethylene lower. It is likely that similar results would be found for the methylated silylenes. Replacement of the methyl group in methylsilylene by a vinyl group preferentially lowers the silylene relative to the doubly bonded system, 1-silaallene. This is consistent with the discussion of the previous section since the bond-separation reactions for vinylsilylene and 1-silaallene are endothermic and exothermic, respectively. The remaining two silylenes in Table III are much more stable than their multiply bonded counterparts. This is not surprising since in reaction 5 the 1,2-shift yields a strained ring containing a C═Si double bond, and in reaction 6 the product is the rather unstable C≡Si triple bond.

The remaining seven reactions in Table III involve 1,2 shifts in carbenes. In striking contrast to the silylenes, these reactions are strongly exothermic, an indication that carbenes are rather unstable. Moreover, for the simplest reaction 7, addition of the MP2 correction further destabilizes ethylidene relative to ethylene. The conversion of the cyclic carbene to silacyclopropene (reaction 12 in Table III) is as exothermic as reaction 7. This is another indication[9] of the unusual stability of silacyclopropene. In contrast, the rearrangement of the same cyclic carbene to the silacyclopropene with the silicon in the base (reaction 13 in Table III) is the least exothermic of the carbene rearrangements. This is in keeping with the fact that reaction 5 is the most endothermic silylene rearrangement. Since the Si═C double bond is expected to be less stable thermodynamically than C═C, it is not surprising that the 1,2 shift for silyl carbene is less exothermic than that for ethylidene. Similar comments apply to the rearrangements to acetylene and the silaallenes.

C. Silicon vs. Carbon Bonding. It was noted in the Introduction that isomerization reactions can be used to compare bond-energy differences for carbon and silicon. A simple example of this is the isomerization of dimethylsilane to ethylsilane:[20]

$$\mathrm{CH_3SiH_2CH_3 \rightarrow CH_3CH_2SiH_3} \qquad \Delta E\ (6\text{-}31\mathrm{G}^*//3\text{-}21\mathrm{G}) = 10\ \mathrm{kcal/mol} \qquad \mathrm{(III)}$$

Assuming transferability of bond types, eq III can be rewritten as

$$\mathrm{BE(CH) - BE(CC) = BE(SiH) - BE(SiC) + 10\ kcal/mol} \qquad \mathrm{(IV)}$$

To the extent that the transferability assumption is reasonable, eq IV implies that the SiH and SiC bond energies are 10 kcal/mol closer than CH and CC. If one uses typical CC and CH bond energies of 80 and 99 kcal/mol, respectively,[21] one would calculate the SiH − SiC differences to be 9–10 kcal/mol. The bond-separation reactions for dimethyl- and ethylsilane can be used to estimate the validity of assuming transferable bond types. The bond-separation energies for these molecules are reasonably small: −0.1 and −1.8 kcal/mol for dimethylsilane and ethylsilane, respectively.

The effect of unsaturation on eq IV can be investigated by considering two methylated silaethylenes:[16]

$$\mathrm{CH_3SiH{=}CH_2 \rightarrow CH_3CH{=}SiH_2} \qquad \Delta E = 8.5\ \mathrm{kcal/mol} \qquad \mathrm{(V)}$$

$$\mathrm{BE({=}C{-}H) - BE({=}C{-}C) = BE({=}SiH) - BE({=}Si{-}C) + 8.5\ kcal/mol} \qquad \mathrm{(VI)}$$

Note that the only assumption in eq VI is that X–H bonds are transferable. Apparently, adjacent unsaturation reduces the carbon vs. silicon difference. This latter effect is augmented if the double bonds are replaced by triple bonds:

$$\mathrm{CH_3Si{\equiv}CH \rightarrow CH_3C{\equiv}SiH} \qquad \Delta E = 4.4\ \mathrm{kcal/mol} \qquad \mathrm{(VII)}$$

$$\mathrm{BE({\equiv}C{-}H) - BE({\equiv}C{-}C) = BE({\equiv}SiH) - BE({\equiv}SiC) + 4.4\ kcal/mol} \qquad \mathrm{(VIII)}$$

A direct comparison involving double bonds can be obtained by using the two silaallenes:

$$\mathrm{H_2C{=}C{=}SiH_2 \rightarrow H_2C{=}Si{=}CH_2} \qquad \Delta E = 21.2\ \mathrm{kcal/mol} \qquad \mathrm{(IX)}$$

$$\mathrm{2[BE({=}C{-}H) - BE({=}Si{-}H)] = BE(C{=}C) - BE(C{=}Si) - 21.2\ kcal/mol} \qquad \mathrm{(X)}$$

According to eq 10, even if the two ═X—H bond energies are identical, the C═C bond is more than 20 kcal/mol stronger than C═Si. If, as seems more likely, BE(═C—H) is 5–10 kcal/mol larger than BE(═Si—H), the C═C bond will be 30–40 kcal/mol stronger than C═Si.

Equations VI and X can be combined to yield another interesting relationship:

$$\mathrm{2BE({=}Si{-}C) - BE(Si{=}C) = 2BE({=}C{-}C) - BE(C{=}C) + 38.2\ kcal/mol} \qquad \mathrm{(XI)}$$

According to this, a Si–C single bond is much closer in energy to Si═C than is a C–C single bond to C═C.

Now consider the isomerization[16]

$$\mathrm{CH_3SiH{=}CH_2 \rightarrow SiH_3CH{=}CH_2} \qquad \Delta E = 17.3\ \mathrm{kcal/mol} \qquad \mathrm{(XII)}$$

In terms of bond energies this may be written

$$\mathrm{3[BE(CH) - BE(SiH)] + [BE(C{-}Si{=}) - BE({=}C{-}Si)] = [BE({=}CH) - BE({=}SiH)] + [BE(C{=}C) - BE(C{=}Si)] + 17.3\ kcal/mol} \qquad \mathrm{(XIII)}$$

If the second term on the left-hand side of eq XIII is approximately zero, eq X and IV may be combined with eq XIII to yield

$$\mathrm{BE(C{=}C) - BE(Si{=}C) = 2[BE(CC) - BE(SiC)] + 15.5\ kcal/mol} \qquad \mathrm{(XIV)}$$

An analogous relation for triple bonds may be obtained by using the isomerization

$$\mathrm{CH_3{-}Si{\equiv}CH \rightarrow SiH_3{-}C{\equiv}CH} \qquad \Delta E = -61.9\ \mathrm{kcal/mol} \qquad \mathrm{(XV)}$$

In terms of bond energies eq XV becomes

$$\mathrm{BE(C{\equiv}C) - BE(C{\equiv}Si) = 3[BE(CH) - BE(SiH)] + [BE({\equiv}Si{-}C) - BE({\equiv}C{-}Si)] + 61.9\ kcal/mol} \qquad \mathrm{(XVI)}$$

Again, taking the second term on the right-hand side of eq XVI to be approximately zero and using eq IV we have

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(20) For dimethyl- and ethylsilane all-trans configurations were assumed.

(21) V. I. Vedeneev, L. V. Gurvich, V. N. Kondrat'ev, V. A. Medvedev, and E. L. Frankenvich, "Bond Energies, Ionization Potentials, and Electron Affinities", Edward Arnold Publishing Co., New York, 1966.

$$\mathrm{BE(C{\equiv}C) - BE(C{\equiv}Si)} = 3[\mathrm{BE(C{-}C) - BE(C{-}Si)}] + 91.9\ \mathrm{kcal/mol} \quad \text{(XVII)}$$

The implications of eq XIV and XVII are striking, even in view of the approximations involved. While eq XIV implies that the difference between a C=C and a C=Si bond is somewhat more than twice that between the corresponding single bonds, the triple bond difference is far greater than three times the single bond difference. This is yet another indication of the strong thermodynamic instability of a C≡Si triple bond.

To illustrate the points made in the previous paragraph, note that current estimates[22] of Si–C bond strengths place them within 5 kcal/mol of C–C bond strengths. Use of eq XIV then indicates that BE(C=C) - BE(C=Si) ≃ 25 kcal/mol. On the other hand, BE(Si—C) would have to be 7–8 kcal/mol greater than BE(C—C) for eq XIV to predict similar double bond energies for the two systems. This appears to be rather unlikely. Using a similar line of reasoning and eq XVII, one concludes that BE(Si—C) would have to be at least 30 kcal/mol greater than BE(C—C) before similar triple bond energies would be predicted. While more accurate calculations are likely to modify the numerical results in XIV and XVII, the qualitative conclusions are likely to hold up.

V. Conclusions

The evidence presented here, coupled with accumulating evidence from a variety of sources, allows us to make some general comments with regard to the relative "stabilities" of multiple bonds containing silicon vis-à-vis those involving carbon only. Since the strength of the silicon–carbon single bond is not well known, we will avoid absolute values for bond stability in the usual sense and discuss only the additional stability which the π electrons provide to the bond in question. This will be contrasted to other alternatives available to the same electrons.

For hydrocarbon systems, the carbon–carbon single bond is strengthened by the addition of π bonds. This process, however, occurs with a net energy cost, as is evidenced by the generally exothermic hydrogenation energies found for isolated multiple bonds (cf. the heats of formation for ethane, ethylene, and acetylene[22]).

Our focus for silicon involved in π bonding is similar in that we try to determine the energy cost of this involvement. The hydrogenation energies of π bonds involving silicon have been found[8] to be more exothermic for Si=C and Si≡C than for the corresponding hydrocarbons. A dramatic increase in hydrogenation energy was noted for the addition of a second π bond to silicon. This increase was considerably larger than would have been expected by comparing C≡C with C=C. The implications of this observation are pointedly reinforced by the results of Table I, which clearly shows the decreasing stability due to increasing the number of π bonds to silicon. This decrease in stability results whether the additional π bond is associated with a triple bond or with two adjacent double bonds. It appears that in acyclic unsaturated hydrocarbons containing silicon, the fewer the number of formal π bonds to silicon, the more stable the isomer. Carbon is apparently more capable of accommodating unsaturation than is silicon.

For the current level of calculation, the foregoing generality is followed for all isomers considered; however, the magnitudes of energies favoring C=C over Si=C are not huge (cf. eq XIV). Indeed, there are examples in the literature[24] which show Si=C to be *kinetically* favored over C=C. While this does not bear directly on the *thermodynamic* stability under discussion here, such kinetic effects would be unlikely if there were a large energy difference favoring C=C over Si=C.

The situation for Si≡C is quite different (cf. eq XVII). Here the relative calculated energy cost is always high—so high, in fact, that $R_2C{=}Si$ competes favorably with RC≡SiR. Moreover, it is difficult to find a well-documented case for Si≡C, even as a reactive intermediate, in the literature. There is reasonable evidence for the existence of C=Si=C,[25] which these calculations suggest is similarly unstable. This does not rule out such possibilities, but rather suggests that alternate structures, considered to be unlikely in carbon chemistry, must be considered. This is a direct consequence of the apparent inherent instability of multiple π bonds to silicon.

Other conclusions which may be drawn from this work are: (1) methyl substitution stabilizes Si=C relative to H; (2) vinyl substitution stabilizes R_2Si: relative to methyl substitution; (3) cyclic silylenes are relatively less strained than their cyclic isomers; and (4) energy differences between silylenes and their π-bonded isomers are much smaller than energy differences between comparable carbenes and their unsaturated isomers.

Two final points are worth mentioning. First, this work has been oriented entirely toward thermodynamic considerations. Since most of the isomers considered here are likely to be, at most, reactive intermediates and since the reactive intermediate which is formed initially will depend on the particular reaction, it is clearly of interest to consider the actual isomerization pathways, particularly the transition states separating pairs of isomers. Second, since it may well be of interest to design reactions which will preferentially yield a particular type of isomer, it is important to investigate the effects of substituents of varying electronegativity on the conclusions drawn here. Studies along both of these lines have been initiated in this laboratory.

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