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Methylsilylene, Silaethylene, and Silylmethylene: Energies, Structures, and Unimolecular Reactivities

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Abstract: The geometries of the lowest singlet and triplet states of methylsilylene, CH_3SiH, and silylmethylene, SiH_3CH, have been optimized at the double-ζ self-consistent field level of theory. Methylsilylene has a singlet ground state with its lowest triplet 19 kcal/mol higher in energy according to the most extensive calculations including CI. Silylmethylene possesses a triplet ground electronic state with a low-lying singlet state at 25 kcal/mol. At the double-ζ SCF level of theory, singlet methylsilylene is predicted to be 11.6 kcal/mol lower in energy than singlet silaethylene. The inclusion of d functions on carbon and silicon in the basis set and configuration interaction decrease this energy separation to only 0.4 kcal/mol. Singlet silylmethylene is calculated to be 69 kcal/mol above singlet silaethylene. For the triplet species, methylsilylene is calculated to be more stable than triplet silaethylene with the most reliable result for the energy difference being 19 kcal/mol. Triplet silylmethylene is predicted to lie 7 kcal/mol higher in energy than triplet silaethylene. Singlet methylsilylene has a sharp CSiH angle of 95.9° which increases to 118.9° in the triplet state. The SiCH angle in singlet silylmethylene is calculated to be 113.8°, and this angle opens up to 139.5° in the lowest triplet state. The transition states for the singlet state 1,2-hydrogen shifts connecting silaethylene to methylsilylene and silylmethylene to silaethylene have been rigorously located at the double-ζ SCF level of theory employing gradient methods. Although there is a 13-kcal/mol barrier for the hydrogen shift from singlet silylmethylene to singlet silaethylene at the double-ζ SCF level, both the addition of d functions on carbon and silicon and CI decrease this energy requirement. The most accurate calculations suggest a barrier of less than 3 kcal/mol. Hence, singlet silylmethylene may not be a kinetically stable species relative to the doubly bonded isomer. In contrast, the barrier to the 1,2-hydrogen shift from singlet silaethylene to singlet methylsilylene is indicated to be ~40 kcal/mol. Experimental results on matrix isolated silylmethylenes and on the gas-phase photolysis of methylsilane are discussed in light of the present theoretical predictions.

Introduction

As evidenced, for example, in numerous recent communications[1] in the *Journal of the American Chemical Society*, there has been an upsurge of interest in the thermal and photochemical reactivity of organosilicon compounds. The reactivity and structure of divalent silicon compounds, silylenes, which are formal analogues of carbenes have recently been reviewed by Gaspar.[2] Interest also remains high in the study of multiply bonded group 4 elements[3] and especially in the silicon–carbon double bond in silaethylenes.[4] The present study examines in detail the connections between silylmethylene, silaethylene, and methylsilylene.

Experimental Background

In understanding the geometries and singlet–triplet energy gaps of substituted methylenes and silylenes, it is of considerable value to compare the results with those of the prototype molecules, CH_2 and SiH_2. Methylene has a triplet ground state with a CH bond length of 1.08 Å and an angle[6-8] of 136 ± 5°. Its lowest singlet state has r(CH) = 1.11 Å and angle (HCH) = 102.4°.[9] SiH_2 has been shown in a rather direct manner by photoelectron spectrometry to have a singlet ground state.[10] A singlet ground state for silylene had also been inferred previously.[11,12] The singlet ground-state geometrical parameters[13,14] are R(SiH) = 1.516 (3) Å and $\angle$(HSiH) = 92.1°. No spectral evidence for triplet silylene has been found although it has been sought.[13]

The singlet–triplet energy separation in methylene is still the subject of some experimental controversy.[15] A photodetachment measurement[16] on CH_2^- gives a singlet–triplet energy gap of 19.5 kcal/mol while experiments based on chemical reactivity,[17] on thermal studies,[18] and on the heat of formation of CH_2 ($^3B_1$) in combination with the threshold for formation of CH_2 ($^1A_1$) in ketene photolysis[19,20] yield a splitting of ~9 kcal/mol. An approximate upper bound to the zero-point triplet energy of SiH_2 was tentatively assigned[10] as $T_0(^3B_1) < 14$ kcal/mol in a laser photoelectron study of SiH_2^-.

A number of experimental studies on substituted silylmethylenes have been reported.[21-23] (Trimethylsily)methylene, $(CH_3)_3SiCH$, has been generated photochemically, matrix isolated in argon and characterized by its IR and ESR spectra.[21] The ESR spectra were interpreted as arising from triplet (trimethylsilyl)methylene in which the bond angle at the carbenic center is linear (**1**).

In an earlier study[21] (trimethylsilyl)carbene was generated by thermolysis of (trimethylsilyl)diazomethane in the gas phase and by photolysis in solution. The (trimethylsilyl)methylene thus generated showed a marked tendency to undergo methyl migration

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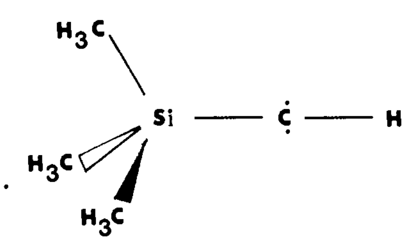

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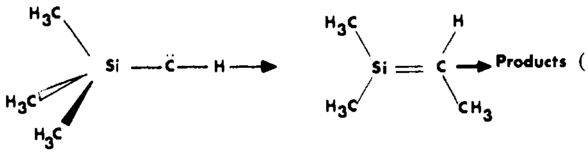
to 2-methyl-2-sila-2-butene and products thereof (eq 1). (Trimethylsilyl)carbene generated under similar reaction conditions[23] was probably formed in a singlet state as evidenced by its stereospecific addition to *trans*-but-2-ene. 1,1,2-Trimethylsilaethylene[24] has been produced by further photolysis of a photostationary mixture of (trimethylsilyl)diazomethane and (trimethylsilyl)diazirine, trapped in an argon matrix, and characterized by its infrared spectrum.



(1)

In a series of experiments on the photochemistry of saturated silicon compounds, Strausz and co-workers[25-27] have presented evidence for the intermediacy of the three species, silylmethylene, silaethylene, and methylsilylene. $CH_3\ddot{S}iH$, CH_2SiH_2, and SiH_3CH were all postulated[26] as primary intermediates in the gas-phase photolysis of methylsilane at the xenon and krypton resonance lines. The nature of the products pointed to the intervention of two singlet silylene diradicals in the mechanism. Methylsilylene appeared to have a high stability with respect to the unimolecular isomerization to silaethylene. In contrast, it was concluded that the rearrangement (eq 2) was quite rapid since silylmethylene could not be trapped.

$$HC\ddot{S}iH_3 \rightarrow H_2CSiH_2 \qquad (2)$$

Theoretical Background

There have been rather a large number of ab initio calculations[4,29-33] at various levels of sophistication on silaethylene, one isomer of the $SiCH_4$ system. The most elaborate calculations[4,33] predict that the ground state of silaethylene is a closed-shell singlet with the lowest triplet state[5] 38.5 kcal/mol higher in energy. Triplet silaethylene's geometry is predicted[4] to be both twisted about the SiC bond and strongly pyramidalized (rocking angle of 49.7°) at Si. The calculations of this work on two other $SiCH_4$ isomers, methylsilylene and silylmethylene, have been carried out, employing the identical basis sets as in ref 4.

A number of small basis set ab initio SCF studies on methylsilylene and silylmethylene have been published.[34-37] Gordon's minimal basis set SCF work[34] was highly suggestive in pointing out that singlet methylsilylene might be thermodynamically more stable than the doubly bonded isomer, singlet silaethylene. Similar results on the relative stabilities of the singlet and triplet $SiCH_4$ isomers were obtained by Schlegel and co-workers.[36] For the lowest triplet states Strausz et al.[35] predicted that both methylsilylene and silylcarbene were more stable than silaethylene on the basis of STO-4G unrestricted Hartree–Fock SCF calculations. Strausz and co-workers[37] have also investigated the lowest triplet state reaction path for the isomerizations of methylsilylene to silaethylene and on to silylcarbene and found very large barriers. It is likely that substantial energy requirements will remain for these triplet state 1,2-hydrogen shifts at higher levels of theory[38] than the STO-4G UHF SCF method employed by Gosavi et al.[37] Prior to the present study the barriers to the singlet state 1,2-hydrogen shifts (eq 3) had not been predicted.

$$CH_3\ddot{S}iH \rightarrow CH_2SiH_2 \rightarrow HC\ddot{S}iH_3 \qquad (3)$$

When the energies and structures of methylsilylene and silylmethylene are studied, a natural comparison with methylene and silylene presents itself. For CH_2, a large number of very highly sophisticated calculations are available,[39] which predict a triplet stable carbene with a singlet–triplet energy gap of 10–12 kcal/mol. For SiH_2, several ab initio studies of the geometries and singlet–triplet splittings have appeared,[40-42] which all predict a singlet ground state for silylene. The two-configuration "Hartree–Fock limit" value[42] for the singlet–triplet energy gap in SiH_2 is predicted to be 18.6 kcal/mol. Near Hartree–Fock results[42] for CH_2 predict the following geometrical parameters: $^3B_1$, $R(CH) = 1.070$ Å, $\angle(HCH) = 129.5°$; $^1A_1$, $R(CH) = 1.097$ Å, $\angle(HCH) = 102.9°$. Similar calculations[42] on SiH_2 predict: $^3B_1$, $R(SiH) = 1.471$ Å, $\angle(HSiH) = 117.6°$; $^1A_1$, $R(SiH) = 1.508$ Å, $\angle(HSiH) = 94.3°$.

In the present work, fully optimized geometries for both singlet and triplet methylsilylene and silylmethylene have been determined at the double-ζ self-sconsistent field level of theory. The effects of the addition of d functions on silicon and carbon and of extensive valence shell configuration interaction on the relative energies of the $SiCH_4$ isomers have been examined. All calculations have been carried out so as to be comparable with the most accurate previously available results on silaethylene.[4] The use of a simple model[42] involving a two configuration SCF calculation on the singlet state and a one configuration SCF treatment of the triplet state to predict the singlet–triplet energy gap in carbenes and related species has been further studied. The transition-state geometries for the singlet state 1,2-hydrogen shifts connecting methylsilylene to silaethylene and silylmethylene to silaethylene have been rigorously located and characterized by gradient methods at the double-ζ SCF level of theory. The effects of d functions in the basis and of CI on the barrier heights to these unimolecular rearrangements have also been studied.

Theoretical Methods

All calculations involved at least a double-ζ basis set[43-46] which may be described as Si(11s7p)/[6s4p], C(9s5p)/[4s2p], and H(4s)/[2s]. The hydrogen exponents were scaled by a factor of

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Table I. Total Energies of Singlet and Triplet Methylsilylene and Silylmethylene

	methylsilylene		silylmethylene	
level of theory	singlet energy, hartrees	triplet energy, hartrees	singlet energy, hartrees	triplet energy, hartrees
double-ζ (DZ) self-consistent field	−329.01579	−329.00524	−328.89637	−328.95876
double-ζ (DZ) configuration interaction	−329.16781	−329.14659	−329.04203	−329.09229
DZ + d (C, Si) self-consistent field	−329.05138	−329.03921	−328.95639	−329.01311
DZ + d (C, Si) configuration interaction	−329.26174	−329.24561	−329.15109	−329.19439

$(1.2)^2$. Sets of Cartesian d functions centered on C (orbital exponent $\alpha = 0.75$) and Si ($\alpha = 0.60$) were added to this doulbe-ζ basis set following geometry optimization. The basis function derived from $d_{xx} + d_{yy} + d_{zz}$ which has overall s-type symmetry was retained in the basis set.

Singlet and triplet state equilibrium geometries as well as the transition-state structures for the singlet state 1,2-hydrogen shifts were rigorously determined by using SCF gradient methods.[47] Calculations of the triplet state equilibrium geometries employed the recent extension[48] of the force method to restricted Hartree–Fock open-shell wave functions. At the final converged geometries all forces in internal valence coordinates were less than 3×10^{-3} mdyn. Moreover, the tolerance for determining the transition state was set at less than 10^{-6} mdyn to obtain a highly reliable force constant matrix. The transition-state structures were subjected to full harmonic vibrational analyses with the force constants obtained as numerical differences of the analytically evaluated forces.[47] The diagonalization of each force constant matrix yielded one and only one negative eigenvalue as is required for a true transition state.[49]

Two configuration SCF calculations on the equilibrium geometries of the singlet states of methylsilylene and silylmethylene were performed with a modified version of the GVBONE program.[50] In the configuration interaction calculations the six lowest energy SCF molecular orbitals, which correspond to Si(1s2s2p) and C(1s), were frozen. The six highest energy virtual orbitals which are the complementary orbitals to the frozen core were deleted in the CI calculations with the larger DZ + d basis set. All Hartree–Fock interacting[51] singly and doubly excited configurations with respect to the appropriate restricted Hartree–Fock SCF reference configuration were included in the CI expansion. For the equilibrium geometries of the molecules which have C_s symmetry the number of configurations in the expansion were as follows: DZ basis, $^1A'$ 5929, $^3A''$ 7394; DZ + d basis, $^1A'$ 8881, $^3A''$ 11 228. For the singlet state 1,2-hydrogen shift reactions, the transition-state structures possess no elements of symmetry and the number of configurations was 10 585 in the DZ basis set. Both the direct[52,53] and unitary group[54,55] CI programs were used in these calculations. Davidson's formula[56] was applied to the singles and doubles CI results in order to estimate the importance of higher than double excitations, specifically unlinked clusters.

Results and Discussion

Energies. Singlet–Triplet Energy Separations. Total and relative energies of the lowest singlet and triplet states of methylsilylene and silylmethylene are given in Tables I and II. Relative energies of the lowest singlet and triplet states of silaethylene[4] are included in Table II for comparison. At all levels of theory, methylsilylene is predicted to have a singlet and silylmethylene a triplet ground state. Such a result is to be anticipated from consideration of the ground states of the parent molecules, silylene and methylene, and of the relatively benign influence expected of the saturated methyl and silyl substituents. In the SCF calculations, the addition of d functions on C and Si to the basis set leads to a slight stabilization of the closed-shell singlet relative to the open-shell triplet state. For methylsilylene, such an addition to the basis set increases the singlet–triplet gap from 1.0 to 7.6 kcal/mol. In silylmethylene, the singlet state is preferentially stabilized by 3.6 kcal/mol, yielding an energy difference of −35.6 kcal/mol (triplet lower). This stabilization of the singlet states of carbenes relative to the triplets upon the addition of d functions to the divalent carbon is frequently observed.[57,58] Of the six basis functions (including the symmetric s-type combination) built from the Cartesian d functions four are of the proper symmetry to mix with the in plane a′ orbital on the carbene or silylene centers, while by symmetry only two may interact with the out-of-plane a″ orbital which becomes singly occupied in the triplet state. The additional d functions of a′ symmetry slightly bias the SCF results in favor of the closed-shell singlet, where the a′ orbital is doubly occupied, as compared to the triplet where both the relevant a′ and a″ MO are singly occupied.

Table II. Singlet-Triplet Energy Separations in Methylsilylene, Silylmethylene, and Silaethylene[a]

	methylsilylene	silylmethylene	silaethylene
double-ζ (DZ) self-consistent field	6.6	−39.2	13.7
double-ζ (DZ) configuration interaction	13.3	−31.5	31.6
DZ + d (C, Si) self-consistent field	7.6	−35.6	16.7
DZ + d (C, Si) configuration interaction	16.4	−27.2	34.7

[a] A positive sign implies that the singlet state is more stable.

Configuration interaction preferentially stabilizes the closed-shell singlet species which has the greater number of electon pairs. In the case of methylsilylene, CI with the double-ζ basis lowers the energy of the ground-state singlet by 6.7 kcal/mol relative to the triplet state, thus increasing the energy separation to 13.3 kcal/mol. With d functions on C and Si added to the basis set, the CI calculations predict an increase of 8.8 kcal/mol in the singlet–triplet energy gap in methylsilylene from 7.6 kcal/mol at the SCF level to 16.4 kcal/mol with the correlated wave function. In silylmethylene, CI with a double-ζ basis predicts a decrease in the magnitude of the singlet–triplet energy separation of 7.7 kcal/mol from −39.2 (ScF) to −31.5 kcal/mol (CI). A slightly larger decrease of 8.4 kcal/mol is calculated at the DZ + d CI level, giving a separation of −27.2 kcal/mol with the inclusion of electron correlation. Similar effects due to polarization functions and configuration interaction have been noted in the case of silaethylene.[4]

Unlinked cluster effects, arising from higher than double excitations, should also be greater for the closed-shell singlet as opposed to the open-shell triplet state. The methylsilylene singlet

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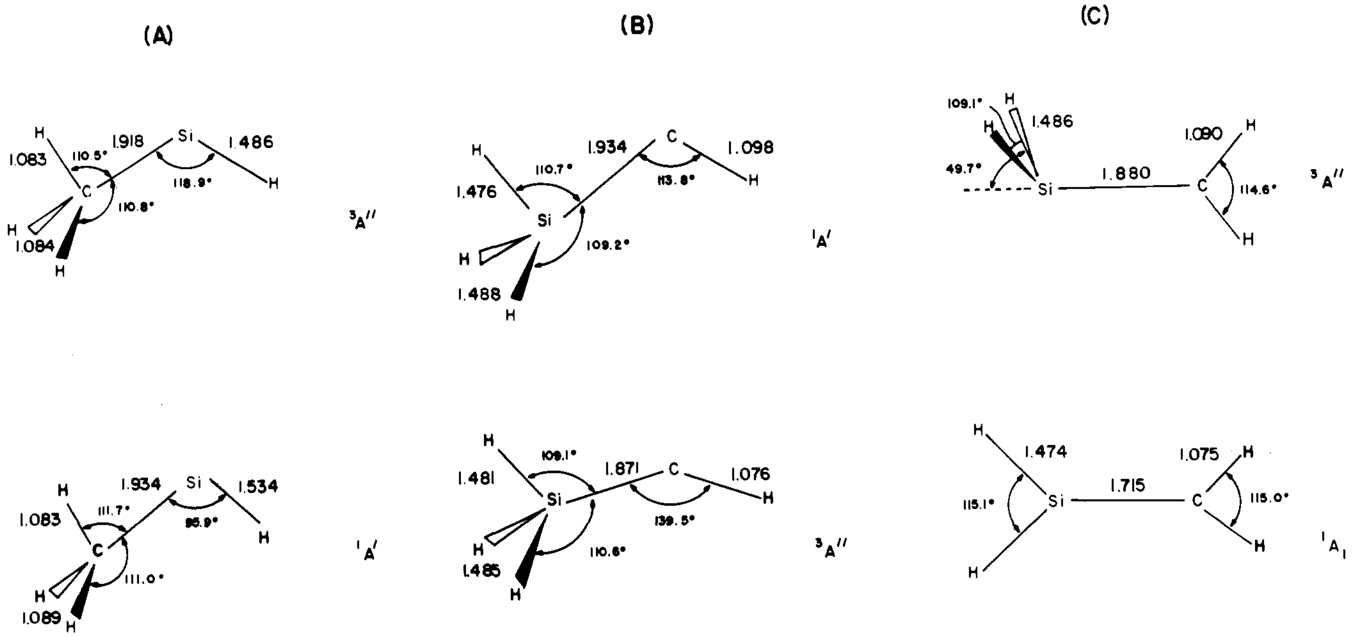
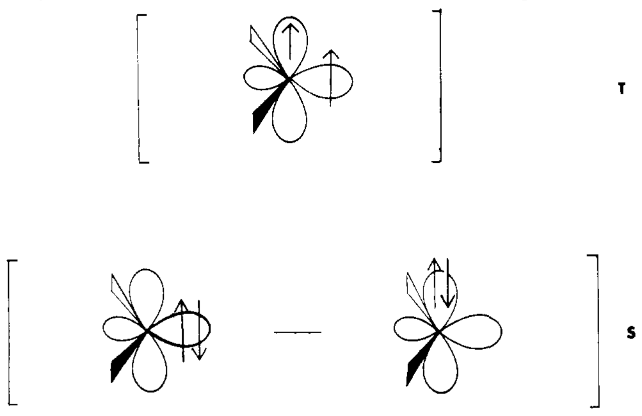


Figure 1. Predicted equilibrium geometries for the lowest singlet and triplet electronic states of (A) methylsilylene, (B) silylmethylene, and (C) silaethylene. The silaethylene structure is that of ref 4.

to triplet energy difference increases from 2.3 to 18.7 kcal/mol by using Davidson's approximate formula[56] to estimate the effects of such higher excitation in the largest DZ + d calculations. A similar correction for silylmethylene stabilizes the singlet state and decreases the energy separation from 27.2 to 24.9 kcal/mol. For silaethylene[4] the higher excitation correction predicted an increase of 3.8 kcal/mol in the singlet–triplet energy gap to yield a final theoretical $E(^3A''-^1A_1)$ of 38.5 kcal/mol. These authors[4] assigned an approximate uncertainty of 5 kcal/mol to this theoretical prediction of the singlet–triplet energy separation in silaethylene. A similar uncertainty in the energy difference may be attached to the final theoretical predictions of this work for the singlet–triplet energy gaps in methylsilylene (18.7 ± 5 kcal/mol) and silylmethylene (−24.9 ± 5 kcal/mol).

There is a fairly well-established theoretical scheme[42,59] which corects for much of the differential correlation energy between the closed-shell singlet and open-shell triplet states of carbenes and related molecules. The triplet state of the carbene or silylene is calculated by the usual one-configuration restricted Hartree–Fock SCF method (OCSCF). However, the closed-shell singlet state of the carbene is described by a two-configuration SCF (TCSCF) wave function in which the two configurations differ only in having the a′ pσ or a″ pπ MO doubly occupied. Such a two-configuration calculation allows the singlet state to mix into its wave function a small amount of character due to having the low-lying a″ pπ MO doubly occupied. A one-configuration SCF treatment of the closed-shell singlet state must completely neglect this low-lying a″ MO.



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Two-configuration SCF calculations were performed on the singlet states of methylsilylene and silylmethylene at the one-configuration SCF optimized geometries. With the DZ + d basis, the total TCSCF energies for the singlet states were as follows: methylsilylene, −329.067 92; silylmethylene, −328.975 44 hartrees. For these species, the weights of the two configurations were as follows: methylsilylene, $0.99[\cdots 10a'^2]-0.11[\cdots 3a''^2]$; silylmethylene, $0.99[\cdots 10a'^2]-0.11[\cdots 3a''^2]$. Employing the TCSCF energies for the singlet states and the one configuration SCF energies for the triplet states, we predicted the singlet–triplet splitting in methylsilylene is predicted to be 17.9 kcal/mol which is in much better agreement with the large scale DZ + d CI result of 16.4 kcal/mol than was the ordinary DZ + d SCF result of 7.6 kcal/mol. For silylmethylene, this scheme predicts a singlet–triplet gap of −23.8 kcal/mol which again is much closer to the large scale DZ + d CI value of −27.2 kcal/mol than was the simple SCF result of −39.2 kcal/mol. If unlinked cluster effects are included in correcting the singlet–triplet energy differences from the DZ + d CI, the agreement of the simple TCSCF singlet–OCSCF triplet scheme is even better. For methysilylene, this model yields a singlet–triplet splitting of 17.9 kcal/mol which is within 0.8 kcal/mol of the final large scale CI + unlinked clusters correction result of 18.7 kcal/mol. A singlet–triplet gap of −23.8 kcal/mol is predicted for silylmethylene by the TCSCF–OCSCF scheme which differs by only 1.1 kcal/mol from the final theoretical value of −24.9 kcal/mol from the large scale CI corrected for higher excitations.

It is also of interest to consider the results on singlet–triplet splittings in terms of substituent effects[60] on this enery gap in the parent molecules, silylene and methylene. It has been argued[60] that electronegative substituents favor the singlet state over the triplet state while electropositive substituents would have the opposite effect. Previous calculations[42] predicted a singlet–triplet energy separation of ~18.6 kcal/mol in SiH_2. The present results indicate that substitution of a methyl group for hydrogen to yield methylsilylene has little effect on the relative energies of the singlet

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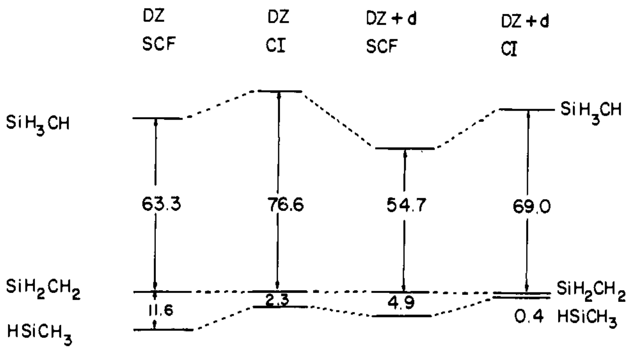
(59) (a) C. F. Bender, J. H. Meadows, and H. F. Schaefer, *Faraday Discuss. Chem. Soc.*, **62**, 59 (1977); (b) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972); (c) C. F. Bender, H. F. Schaefer, D. R. Franceschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972).

(60) (a) C. W. Bauschlicher, H. F. Schaefer, and P. S. Bagus, *J. Am. Chem. Soc.*, **99**, 7106 (1977); (b) J. F. Harrison, R. C. Liedtke, and J. F. Liebmann, *ibid.*, **101**, 7162 (1979).



SINGLET RELATIVE ENERGIES

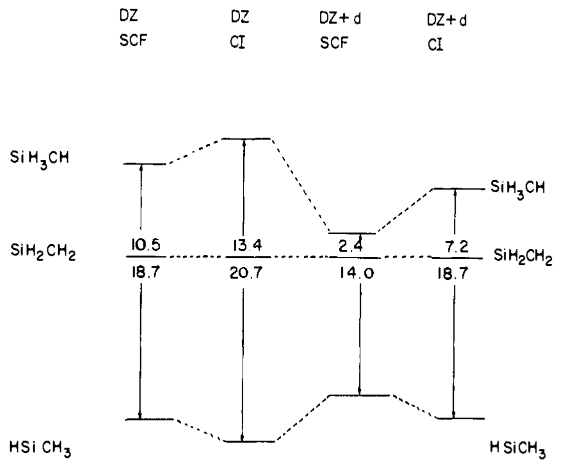
Figure 2. Relative energies of singlet $SiCH_4$ isomers at various levels of theory.

and triplet states since an energy splitting of 18.7 kcal/mol was found. In contrast, methylene has been calculated[39] to have a triplet–singlet splitting of ~10–12 kcal/mol, but subsitution of the electropositive silyl group to give silylmethylene results in a triplet–singlet energy gap of 24.9 kcal/mol.

Relative Stabilities of Methylsilylene, Silaethylene, and Silylmethylene. The energies at various levels of theory of singlet methylsilylene and silylmethylene relative to silaethylene are presented in Figure 2. Singlet silylmethylene is predicted to be much less stable than singlet silaethylene. The DZ + d CI calculation predicts that $^1A'$ silylmethylene lies 69.0 kcal/mol higher in energy than $^1A_1$ silaethylene. The singlet methylsilylene is predicted to be more stable than the doubly bonded isomer, singlet silaethylene, at all levels of theory considered in this work. However, the energy difference decreases from 11.6 kcal/mol at the DZ SCF level to only 0.4 kcal/mol at the DZ + d CI level. Given an estimated uncertainty in these energy differences of perhaps 5 kcal/mol, it is judicious to conclude only that singlet methylsilylene and singlet silaethylene are very close to equal in terms of thermodynamic stability.

Thermochemical arguments may be used to rationalize the predicted stabilities of the singlet $SiCH_4$ isomers. For $SiH_3\dot{C}H$ and CH_2SiH_2 if the assumption is made that the similar bonds (e.g., SiH) in these two molecules have equal energies then the structures differ by one SiH bond in favor of silylmethylene and one CH bond and the π component of the SiC double bond in favor of silaethylene. $D_\pi(Si{=}C)$ has recently been estimated[61] to be 28.8 ± 8 kcal/mol. D(SiH) may be taken as ~85 ± 5 kcal/mol[62] and D(CH) as ~97 ± 3 kcal/mol.[61] With use of these bond energies singlet silaethylene is then predicted to be ~41 kcal/mol more stable than singlet silylmethylene with an uncertainty of perhaps 15 kcal/mol. Moreover, the single SiC σ bond in silaethylene is probably stronger than the SiC σ bond in silylmethylene (e.g., D(C–C) in ethane is ~88 kcal/mol while $D(H_2\dot{C}{-}\dot{C}H_2)$ in ethylene is ~110 kcal/mol,[63] a difference of 22 kcal/mol), further increasing this 41-kcal/mol difference in favor of silaethylene. The present best quantum chemical prediction for this difference is 69 ± 5 kcal/mol.

The present theoretical treatment places singlet methylsilylene very close in energy to singlet silaethylene. In this case an additional CH bond favors the methylsilylene form while an SiH bond and the π component of the SiC double bond favors silaethylene. With use of the bond energies and assumptions given above, singlet methylsilylene would be predicted to lie ~17 kcal/mol higher in energy than singlet silaethylene. However, as has been frequently noted,[64] silicon strongly prefers the divalent to the quadrivalent state which may be reflected in larger SiH and SiC bond energies in methylsilylene as opposed to silaethylene.



TRIPLET RELATIVE ENERGIES

Figure 3. Relative energies of triplet $SiCH_4$ isomers at various levels of theory.

The relative energies of the triplet states of methylsilylene, silaethylene, and silylmethylene are given in Figure 3. At all levels of theory triplet silylmethylene is less and triplet methylsilylene more stable than triplet silaethylene. The DZ + d CI calculations predict $^3A''$ silylmethylene to lie 7.2 kcal/mol higher in energy than triplet silaethylene. The loss of the π component of the SiC double bond in triplet silaethylene along with the predicted triplet stability of silylmethylene of 24.9 kcal/mol accounts for the very marked differences in the relative stabilities of the singlet and triplet states of silylmethylene vs. silaethylene. Triplet methylsilylene is calculated to be 18.7 kcal/mol more stable than triplet silaethylene at the same level of theory.

Structures of Methylsilylene and Silylmethylene. The predicted equilibrium geometries for the lowest singlet and triplet states of methylsilylene and silylmethylene are shown in Figure 1. The silaethylene structure of ref 4 is also illustrated. For singlet methylsilylene, the CSi single bond length is 1.934 Å, which is 0.219 Å longer than the CSi double bond in silaethylene.[4] The SiH distance of 1.534 Å in singlet methylsilylene is in close agreement with a DZ SCF result[42] of 1.533 Å for SiH_2 ($^1A_1$). The CSiH angle in singlet methylsilylene is predicted to be 95.9° which is slightly greater than the calculated[42] (DZ SCF, 94.1°) or experimental (92.1°) angles in silylene. The slight opening up of this angle in methylsilylene as compared to silylene may reflect a greater steric effect due to the methyl group. The CH bond which eclipses the in-plane lone pair on the silylene center has a length of 1.083 Å. The other two CH bonds are slightly longer (1.089 Å) due to hyperconjugative withdrawal of electron density[66] from the π-type group orbital of the methyl group into the empty out-of-plane $p\pi$ orbital on silicon.

The CSiH angle in triplet methylsilylene opens up by 23.0° relative to the singlet state to a value of 118.9°. For SiH_2 at the DZ SCF level of theory[42] the HSiH angle increases by 23.5° on going from the $^1A_1$ to the $^3B_1$ state. The slightly larger angle (1.3°) in triplet methylsilylene as compared to triplet silylene may again be attributed to somewhat greater steric demands of the methyl group relative to hydrogen. The silicon–carbon bond length in triplet CH_3SiH is 1.918 Å, which is 0.016 Å shorter than in the singlet state. The SiH bond also shortens the result of a similar calculation on triplet methylene,[42] 1.071 Å (experimental 1.08 Å). The three SiH bond lengths in the silyl group of triplet silylmethylene are nearly equal just as were the three CH bonds

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[61] L. E. Gusel'nikov and N. S. Nametkin, *J. Organomet. Chem.*, **169**, 155 (1979).

[62] The average of the two values used in ref 61.

[63] S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley-Interscience, New York, 1976, p 64.

[64] For example: (a) Reference 31; (b) P. H. Blustin, *J. Organomet. Chem.*, **105**, 161 (1976). (c) J.-C. Barthelat, G. Trinquier, and G. Bertrand, *J. Am. Chem. Soc.* **101**, 3785 (1979); (d) A. C. Hopkinson and M. H. Lien, *J. Chem. Soc., Chem. Commun.*, 107 (1980).

[65] It should be noted that the triplet geometries in ref 34 were not fully optimized but rather estimated on the basis of expected changes in the optimized singlet state geometries. In addition, in both ref 34 and 35 the geometry used for triplet silaethylene differs considerably in the SiH_2 rocking angle from that of ref 4 or ref 33.

[66] R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972).

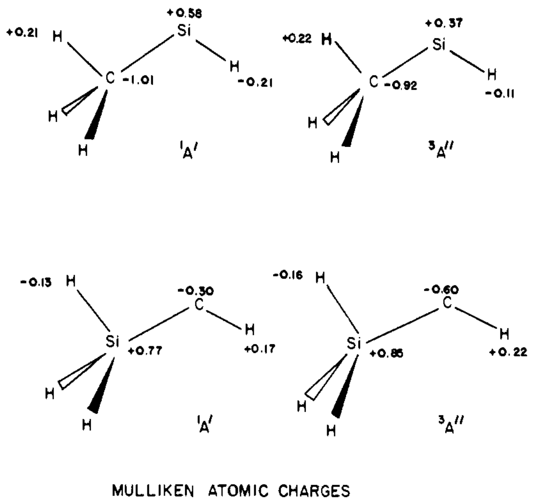

Figure 4. Net atomic charges from Mulliken population analyses on methylsilylene and silylmethylene (DZ + d basis set).

in the methyl group in triplet methylsilylene.

Singlet silylmethylene has a SiCH angle of 113.8° which is 25.7° less than in the triplet state. For CH_2 the experimentally observed change in this angle is somewhat greater than in silylmethylene. In $^3B_1$ CH_2, the HCH angle is 134 ± 2°[6,8] and this value decreases by over 30–102.4°[9] in the $^1A_1$ state. It seems clear that the steric bulk of the silyl group prevents the singlet state of silylmethylene from becoming as sharply bent as does singlet methylene. The SiC bond length in singlet silylmethylene is 1.934 Å (the same value as in methylsilylene) which is 0.063 Å greater than in the triplet state. The CH bond length in $^1A'$ SiH_3CH is 1.098 Å and has increased by 0.22 Å from its value in the triplet state. The SiH bonds in the silyl group show a dramatic lengthening of the gauche SiH bonds relative to the trans SiH bond. The empty pπ-type MO on the carbenic center steals electron density from the π-group orbital of the silyl group which is bonding in both gauche SiH bonds.

Certain structural features of the three $SiCH_4$ isomers may be compared. The SiC bond lengths for the triplet species decrease from methylsilylene (1.918 Å) to silaethylene (1.880 Å) to silylmethylene (1.871 Å). A similar trend was predicted by the small basis set SCF calculations.[35] The SiH bond lengths in all the triplet isomers are nearly equal, ranging from 1.481 to 1.486 Å. In the singlet isomers the SiC bonds in methylsilylene and silylmethylene are 0.219 Å longer than the double bond in silaethylene.

Charge Distributions. The net atomic charges derived from Mulliken population analyses on methylsilylene and silylmethylene are illustrated in Figure 4. Results from the DZ + d SCF calculations for both the singlet and triplet states are shown. In all four cases, the carbon atom bears a net negative atomic charge and the silicon atom a net positive charge. Such a charge distribution would be anticipated from consideration of the electronegatives for C (2.55) and Si (1.90).[67] It should be noted that C is more but Si less electronegative than H (2.20 on the same scale). Thus, hydrogens attached to silicon in the silyl group or at the silylene center bear net negative atomic charges.

In all four species, the total d orbital atomic populations are small (0.10 electron or less). d orbitals have the largest atomic population for the carbon in singlet and triplet methylsilylene. Although somewhat arbitrary due to the nature of the population analysis, the relatively small d orbital populations do not provide evidence for any "special" d orbital effects in these systems. The double-ζ population analyses, which are not shown, illustrate exactly the same trends as in the calculations including d functions. In the DZ basis, Si bears a slightly larger net positive charge (~0.05 electron) and the hydrogens attached to silicon are slightly more negative (~0.01 electron).

Table III. Calculated Barrier Heights (in kcal/mol) for the Singlet State 1,2-Hydrogen Shift Reactions

	silaethylene to methylsilylene	silylmethylene to silaethylene
double-ζ (DZ) self-consistent field	45.0	13.1
double-ζ (DZ) configuration interaction	43.4	3.2
DZ + d (C, Si) self-consistent field	44.6	8.4
double-ζ (DZ) configuration interaction with Davidson's correction	41.0	1.9

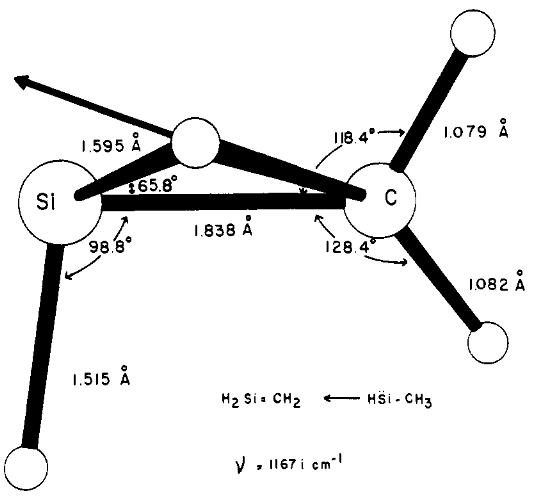

Figure 5. The transition-state structure for the unimolecular rearrangement of singlet methylsilylene to singlet silaethylene. The normal mode associated with motion along the reaction coordinate is also illustrated.

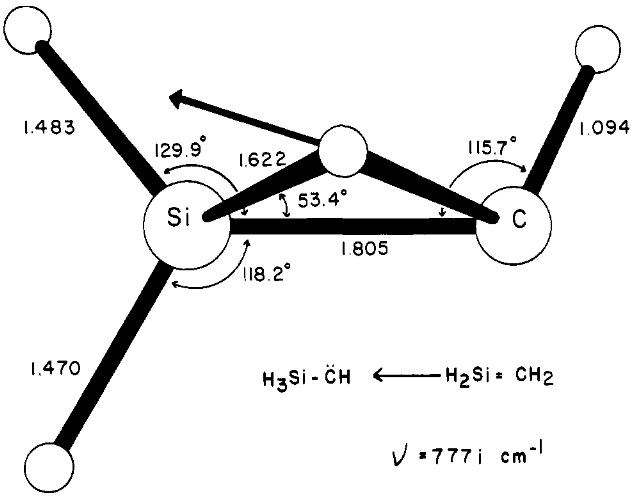

Figure 6. The transition-state structure for the unimolecular rearrangement of singlet silaethylene to singlet silylmethylene. The normal mode associated with motion along the reaction coordinate is also illustrated.

Unimolecular Reactivities. The Rearrangement of Silaethylene to Methylsilylene. The barrier heights at various levels of theory for the singlet state 1,2-hydrogen shift reaction connecting silaethylene to methylsilylene are given in Table III. All calculations were performed at the DZ SCF optimized geometries. The transition-state structure and the normal mode with frequency 1167i cm^{-1} associated with motion along the reaction coordinate are illustrated in Figure 5.

Viewing the reaction as proceeding from singlet silaethylene to singlet methylsilylene the barrier decreases by 1.6 kcal/mol when electron correlation effects are included at the double-ζ level.

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[67] A. L. Allred. *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

The inclusion of d functions on C and Si decreases the SCF barrier very slightly (0.4 kcal/mol). The approximate correction for higher excitations[56] also leads to a decrease in the barrier from 2.4 to 41.0 kcal/mol. However, if the reaction is viewed in the sense of methylsilylene rearranging to silaethylene the change in the relative energies of the stable species (Figure 2) means that the barrier decreases from 56.6 kcal/mol at the DZ SCF level to 43.8 kcal/mol at the DZ + CI level.

The transition-state geometry lacks any element of symmetry and resembles the methylcarbene to ethylene rearrangement transition state[5] in that it is probably[68] a hydrogen initially gauche to the hydrogen attached to silicon in methylsilylene which undergoes the migration. The SiC distance in the transition state geometry is 1.838 Å which is nearly halfway between its value in silaethylene (1.715 Å) and methylsilylene (1.934 Å). The $CSiH_1$ angle of 98.8° in the transition state is only very slightly larger (2.9°) than the equilibrium value in methylsilylene and the SiH_1 distance of 1.515 Å is 0.019 Å shorter than its value in methylsilylene but 0.041 Å longer than in silaethylene. Thus, the silaethylene to methylsilylene transition state structure is "late" in several of the geometric parameters involving the silicon atom.

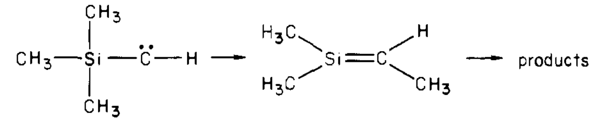
The Rearrangement of Silylmethylene to Silaethylene. The calculated barrier heights are given in Table III and the transition-state geometry and the reactive normal mode of frequency 777i cm^{-1} illustrated in Figure 6.

The barrier decreases from 13.1 kcal/mol at the DZ SCF level of theory to 8.4 kcal/mol at the DZ + d SCF level. CI in the DZ basis yields a barrier of only 3.2 kcal/mol. Applying Davidson's correction[56] to the DZ CI energy results on singlet silylmethylene and singlet silaethylene reduces the rearrangement barrier to only 1.9 kcal/mol. Given the rather small barrier height along with the fact that the geometry was determined only at the DZ SCF level, it is not clear that singlet silylmethylene is, in fact, a stable species.

The transition-state geometry for the silylmethylene to silaethylene rearrangement is early in the CH_1 distance (1.094 Å vs. 1.098 Å in the reactant and 1.075 Å in the product) and in the $SiCH_1$ angle (115.7° vs. the reactant's 113.8° and the product's 122.25°). However, the SiC bond has shortened in the transition-state structure to 1.805 Å which lies closer to the product silaethylene (1.715 Å) than the reactant silylmethylene (1.934 Å). Again, it is probably one of the hydrogens gauche to the methine hydrogen which migrates. Migration of the trans hydrogen in either singlet silylmethylene or methylsilylene is unfavorable as *two* electron pairs (the CH or SiH bond pair and the in plane lone pair on the carbene or silylene center) are brought into the same region of space. The migration of one of the gauche hydrogens on the other hand is initially toward the low-lying empty $p\pi$ molecular orbital on the carbene or silylene center.[69]

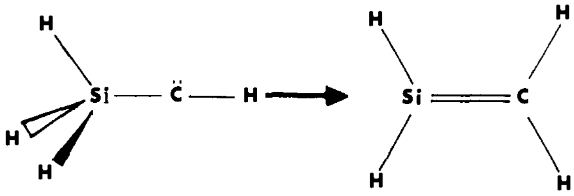
Comparisons with Experimental Results. The present calculations may profitably be compared with experiment on a number of points. Drahnak et al.[28] present evidence that $(CH_3)_2\ddot{Si}$ has a singlet ground state. The present result that $(CH_3)\ddot{Si}H$ is a ground-state singlet with the lowest triplet state 18.7 kcal/mol higher in energy provides indirect support for the assignment of a singlet ground state to $(CH_3)_2\ddot{Si}$. Kasden et al.[10] tenatively assign $T_0(^3B_1)$ in SiH_2 as ≤13.8 kcal/mol. The present calculations predict that in methylsilylene the singlet–triplet energy gap is 18.7 kcal/mol in reasonable agreement with the experimental value in silylene although somewhat larger. It might be noted that previous ab initio calculations[42] on SiH_2 predicted a singlet–triplet energy separation of 18.6 kcal/mol which is 4.8 kcal/mol larger than the experimental value.

Certain experimental studies on the thermolysis and photolysis of (trimethylsilyl)diazomethane have indicated that methyl migration from Si to C in the silylcarbene or carbene like species is a facile process (eq 4). Indirect support for the ease of such



(4)

a rearrangement may be found in the very small calculated barrier (<3 kcal/mol) to the singlet state rearrangement of silylmethylene to silaethylene (eq 5). Although methyl migration should be more difficult than hydrogen migration, the very small barrier to the 1,2-hydrogen shift may be indicative of a relatively small barrier to the 1,2-methyl shift.



(5)

Chedekel and co-workers[21] have matrix isolated triplet (trimethylsilyl)methylene and characterized it as a linear carbene on the basis of its ESR spectrum. The present calculations indicate that the parent system, silylmethylene, definitely has a triplet ground state with the singlet ~25 kcal/mol higher in energy. The SiCH bond angle in triplet silylmethylene is quite large at 139.5°. The substitution of methyl groups for hydrogen in (trimethylsilyl)methylene and/or the influence of the matrix could lead to a value for this angle near 180° as deduced from experiment. In addition, the smaller STO-4G UHF SCF calculations[35] indicated a barrier of only 5.5 kcal/mol to inversion at the triplet carbene center in methylsilylene. Triplet methylsilylene may be "quasilinear". However, it should be noted that weakly bent carbene species in matrices may give ESR parameters which suggest that the molecule is linear.[10]

In the high-energy gas-phase photolysis of methylsilane (CH_3SiH_3) Strausz and co-workers[25,26] interpreted their results as involving all three species, $CH_3\ddot{Si}H$, CH_2SiH_2, and $SiH_3\ddot{C}H$, as primary intermediates. Methylsilylene was found to be highly stable with respect to unimolecular isomerization to silaethylene. This result finds strong support in the present work, in which the calculated barrier to

$$H\ddot{Si}CH_3\ (^1A') \rightarrow H_2SiCH_2\ (^1A_1) \qquad (6)$$

is ~40 kcal/mol. On the other hand, singlet silylmethylene was postulated to undergo a very rapid rearrangement (eq 7) since

$$H\ddot{C}SiH_3\ (^1A') \rightarrow H_2C{=}SiH_2\ (^1A_1) \qquad (7)$$

no singlet silylmethylene products could be trapped. The present calculations indicate that there is either a very small (<3 kcal/mol) or perhaps even no barrier to the highly exothermic (69 kcal/mol) rearrangement of silylmethylene ($^1A'$) to silaethylene ($^1A_1$).

Concluding Remarks. The most striking results of the present extensive calculations are a confirmation of the near degeneracy in energy of the ground states of methysilylene and silaethylene (within 1 kcal/mol) and the prediction of a large barrier (~40 kcal/mol) to the 1,2-hydrogen shift connecting these two isomers. Silylmethylene ($^1A'$) lies much higher in energy (~69 kcal/mol) than silaethylene ($^1A_1$), and there is only a very small barrier to its rearrangement to the doubly bonded isomer.

From a technical viewpoint, the consistent accuracy of the two-configuration SCF singlet and one-configuration SCF triplet model for singlet–triplet splittings in methylenes and silylenes relative to large scale CI results should be noted.

Acknowledgment. The support of this work by the National Science Foundation and by the Robert A. Welch Foundation is gratefully acknowledged.

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(68) Although it certainly appears that it is a gauche hydrogen which migrates, since the reaction pathway has not been followed in these calculations, some complex motion before or beyond the transition-state geometry cannot be completely ruled out.

(69) Reference 5b discusses the somewhat analogous rearrangement of singlet methylcarbene to singlet ethylene in terms of MO following arguments using MO obtained from ab initio calculations.

(70) (a) A. Dendramis and G. E. Leroi, *J. Chem. Phys.*, **66**, 4334 (1977). (b) For a theoretical study on cyanomethylene related to this point, see: M. E. Zandler, J. D. Goddard, and H. F. Schaefer, *J. Am. Chem. Soc.*, **101**, 1072 (1979).