ditional stabilization relative to **4**. In fact, constraining the hydrogens to lie perpendicular to the Si–Si bond causes the Si–Si bond distance to increase to 2.346 Å, presumably due to repulsion between the hydrogen and silicon valence s orbitals.

Folding along the Si–Si bond, which results in structure **1**, reduces this repulsion, leading to a Si–Si bond distance of 2.181 Å. In this conformation the π-like orbitals (π_x and π_y if the Si–Si bond is oriented along the z axis) simultaneously serve in Si–Si and Si–H bonding.

The stepwise distortion from structure **6** to **1** is accompanied by an interesting change in the energies of the π orbitals. In structure **6** the highest occupied orbitals are π_x and π_y. This ordering is preserved in structure **4** although there is some participation of one of the π orbitals in bonding with the hydrogens. Further distortion to the planar bridged conformation results in significant stabilization of the π orbital that is in the plane of molecule (i.e., involved in bonding with the hydrogens). Distortion from D_{2h} to C_{2v} is accompanied by further stabilization of the remaining π orbital. When viewed in this manner, the anomalous bonding is bridged Si_2H_2 results from a drive toward better participation of the silicon valence p orbitals in π-like bonding.

IV. Conclusions

Clearly the Si_2H_2 hypersurface exhibits unusual characteristics. The absence of a stable linear form of disylyne is a striking feature and indicates that silicon is unwilling to participate in triple bonds. The span of relative energies for the stable Si_2H_2 conformations is much smaller than that of the C_2H_2 species (32.1 kcal mol^{-1} vs. 97.3 kcal mol^{-1}).

These calculations at the MP4/6-31++G**//HF/6-31G** level of theory suggest that the ground state of Si_2H_2 is the bridged form (**1**). Both the C_2H_2 and Si_2H_2 molecular systems were found to possess stable "vinylidene" (**2**, **8**) and bridged (**1**, **9**) conformations. With respect to the Si_2H_2 species, determination of the geometry using the electron correlated MP2/6-31G** approach does not modify these conclusions; linear $D_{\infty h}$ disilyne corresponds to a transition structure while bridged disilyne was found to be a minimum on the Si_2H_2 potential surface. The bridged form of C_2H_2 was found to exist although it is significantly less stable relative to acetylene than is vinylidene.

Several stable conformations with triplet electronic states exist on both the C_2H_2 and Si_2H_2 hypersurfaces. In the case of the C_2H_2 species there is a clear preference for planar structures while all the Si_2H_2 triplets were found to be nonplanar.

On the basis of comparisons with the calculations performed by Snyder et al.[15] it is clear that polarization functions are required in describing compounds such as these. The energy orderings predicted for the Si_2H_2 singlets are unaltered by inclusion of electron-correlation effects provided that the bais set contains polarization functions. This indicates that an adquate basis set is essential in obtaining reliable relative energies.

Registry No. 2, 87970-40-9; 6, 36835-58-2; 7, 74-86-2; 8, 2143-69-3.

Theoretical Study of Methylsilanone and Five of Its Isomers

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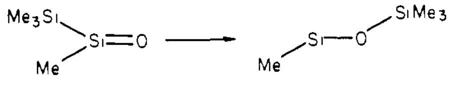
Abstract: By use of 3-21G SCF geometries and relative energies from MP3/6-31G* wave functions, methylsilanone has been found to be the most stable of the six isomers investigated. The relative stabilities of methylsilanone and silylformaldehyde are rationalized by the metathesis reaction $H_2SiO + C_2H_4 \rightarrow H_2CO + H_2CSiH_4$. This reaction is used to suggest that the C=O bond is about 10 kcal/mol stronger than Si=O.

Introduction

There has recently been considerable experimental[1-7] and theoretical[8] interest in silene to silylene rearrangements. Recently, Barton and co-workers[9] investigated the analogous silanone rearrangement



(1)

in which a Si=O double bond rearranges to the corresponding silylene. Based on their experimental evidence, the authors concluded that reaction 1 does not readily occur. In addition, it has been postulated[1] that a silene and a ketone may undergo a metathesis reaction

$$R_2Si{=}CR_2 + R_2C{=}O \rightarrow R_2Si{=}O + R_2C{=}CR_2 \quad (2)$$

to form a silanone and the corresponding alkene.

Reactions 1 and 2 suggest that it would be interesting to investigate the relative energies of the two isomers in (1) as well as the isomeric substituted formaldehyde and hydroxy-substituted silenes. Moreover, a reliable calculation of the energy difference in (2) will provide an estimate of the energy difference beteen the Si=O and Si=C bonds. To minimize the computational effort, the present work presents calculations on $CH_3SiH{=}O$ and five of its isomers.

Computational Methodology

Except for tests with larger basis sets for H_2SiO, all geometries were calculated by use of the 3-21G basis set[10] and the Schlegel

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Table I. Properties of H_2SiO[a]

	R_{SiO}	R_{SiH}	∠HSiO	total energy, au	dipole moment, D
3-21G	1.559	1.475	123.0	−362.95589	3.89
6-31G*	1.502	1.475	124.4	−364.91214	4.18
JKS SCF[b]	1.485	1.472	125.0	−364.7344	4.43
CEPA[b]	1.507	1.471	125.0	−365.0743	
MP2/6-31G*//3-21G[c]				−365.18218	
MP3/6-31G*//3-21G[c]				−365.18005	
MP2/6-31G*//6-31G*[d]				−365.18001	
MP3/6-31G*//6-31G*[d]				−365.18027	

[a] Bond lengths in Å, angles in deg. [b] Reference 17 of text. [c] MP2 or MP3 with 6-31G* at the 3-21G geometry. [d] MP2 or MP3 with 6-31G* at the 6-31G* geometry.

Table II. Total Energies (Hartree) of H_4CSiO Isomers

molecule	3-21G	6-31G*	MP2/3-21G	MP3/3-21G
$\mathrm{CH_3SiH{=}O}$	−401.80632	−403.96311	−402.09461	−402.09041
$\mathrm{CH_3{-}\ddot{S}iOH}$	−401.84374	−403.96980	−402.09739	−402.10933
$\mathrm{CH_2{=}SiHOH}$	−401.79663	−403.93825	−402.06188	−402.07171
$\mathrm{SiH_3CH{=}O}$	−401.76525	−403.93682	−402.03501	−402.04530
$\overline{\mathrm{SiH_2{-}CH_2{-}O}}$	−401.76764	−403.92600	−402.03911	−402.04868
$\mathrm{SiH_2{=}CHOH}$	−401.72494	−403.87420	−401.99763	−402.01157

Table III. Relative Energies (kcal/mol) of H_4CSiO Isomers

molecule	3-21G	6-31G*	MP2/3-21G	MP3/3-21G	MP2/6-31G*[a]	MP3/6-31G*[a]
$\mathrm{CH_3{-}SiH{=}O}$	0.0	0.0	0.0	0.0	0.0	0.0
$\mathrm{CH_3{-}\ddot{S}iOH}$	−23.5	−4.2	−1.7	−11.9	17.6	7.4
$\mathrm{CH_2{=}SiHOH}$	6.1	15.6	20.5	11.7	30.0	21.2
$\overline{\mathrm{SiH_2{-}CH_2{-}O}}$	24.2	23.3	36.0	26.2	35.1	25.3
$\mathrm{SiH_3{-}CH{=}O}$	25.8	16.5	37.4	28.3	28.1	19.0
$\mathrm{SiH_2{=}CHOH}$	51.1	57.9	58.2	49.5	65.0	56.3

[a] Assuming additivity of polarization and correlation effects. See text.

method for geometry optimization[11] as implemented in GAUSSIAN80.[12] Single point calculations were performed using the larger 6-31G* basis set[13] and second- and third-order many-body perturbation corrections (MP2 and MP3) as formulated by Moller and Plesset[14] and developed Pople and co-workers.[15] For most molecules the MP/6-31G* energies were estimated by assuming that the correlation and polarization effects are additive. This has been demonstrated by a number of authors[16] and generally is an excellent approximation unless the system being studied exhibits strong configurational mixing.

Results and Discussion

A. Comparison with Previous Calculations: H_2SiO. Jaquet, Kutzelnigg, and Staemmler[17] have pointed out that diffuse basis functions may be important to provide an adequate description of some properties of the SiO bond. Since neither of the basis sets used in this work includes such functions, it is necessary to compare the results of these authors with the predictions of 3-21G and 6-31G* before proceeding to the larger molecules. A number of properties of H_2SiO are summarized in Table I. All levels of theory are in close agreement with their predictions of the SiH bond length and HSiO angle. The 3-21G and 6-31G* predictions for the SiO bond length are not surprising since the latter basis set generally shortens bond lengths, while the addition of correlation effects lengthens them again.[18] Based on previous calculations,[6,16,18] one expects the actual SiO bond to be slightly longer than that predicted by CEPA and 0.03–0.04 Å shorter than the 3-21G value. Note also that the MP3 energies are virtually identical for the 3-21G and 6-31G* structures. This suggests that the energy comparisons given below will not be significantly altered by using 6-31G* geometries. As noted by Jacquet et al.,[17] the addition of diffuse functions tends to increase the polarization of the SiO bond. Thus the 6-31G* charge on oxygen is −0.64, whereas that predicted Jacquet et al. is −0.82. Nevertheless, the dipole moments predicted by the two basis sets are quite similar (see Table I). To summarize, despite small differences in certain predicted properties, the use of 3-21G geometries for the larger molecules of interest does not appear to be unreasonable.

B. Geometries and Charge Densities. The 3-21G geometries and charge densities from 6-31G*//3-21G Mulliken population analyses for the six H_4SiCO isomers are illustrated in Figure 1. Note that the SiO bond length in $\mathrm{CH_3SiH{=}O}$ is identical with that in H_2SiO, so one expects a shortening with more sophisticated wave functions. There is considerable variation in the calculated C–Si distances. The difference between the two substituted silaethylenes is expected based on previous calculations with electronegative substituents on this system.[16] Similarly, the SiC bond length in the silylene structure (**1**) is the same as that in the fluoro analogue[16] and the distance in the epoxide ring (**4**) is only slightly longer than that in silacyclopropane.[19] If the =O moiety is viewed as an electronegative substitutent, the CSi bond lengths in the

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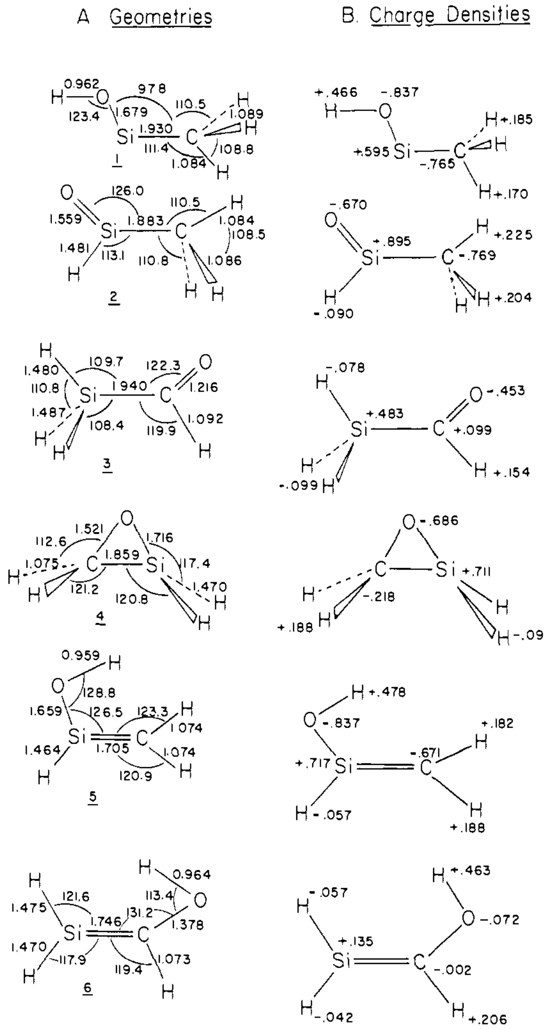


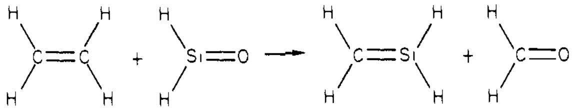
Figure 1. Geometries (3-21G) and charge distributions (6-316*).

remaining isomers are also consistent since substitution at the silicon end shortens the bond, while substitution at carbon has the opposite effect.[16]

The charge distributions are self-explanatory; however, two points are worth noting. First, silicon d orbital populations are small for all six isomers, with the largest d population being 0.34. This is consistent with the results of Jacquet, Kutzelnigg, and Staemmler on H_2SiO.[17] Second, in silyl formaldehyde, there is a net shift in electron density of about 0.2 electrons from the silyl group to HCO. In contrast, the migration in structure **2** is toward the methyl group.

C. Energetics. The total and relative energies of the six H_4CSiO isomers are listed in Tables II and III, respectively. At the SCF level, with either basis set, the most stable structure is found to be the silylene (**2**); however, the addition of polarization functions into the basis set and of correlation contributions into the wave function stabilize the silanone (**1**) relative to **2**. To the extent that these two effects are additive, **1** is predicted to be the most stable structure at the MP2 or MP3 level with a 6-31G* basis set (last two columns of Table III).

Particularly interesting is that $CH_3SiH{=}O$ is found to be more stable than $SiH_3CH{=}O$ at all levels of calculation. In terms of bond energies, one expects the CH bonds in **1** to be stronger than the SiH bonds in **3**, and this will stabilize the former molecule. By similar reasoning, the reverse will be true for the X–H bonds adjacent to X=O (X=C or Si). The geometries in Figure 1 suggest that the C–Si bond in **1** may be strengthened relative to that in **3** due to greater delocalization from the Si=O bond than from the C=O bond. These considerations are incomplete unless one has a comparison of the Si=O and C=O bond strengths. Such a comparison may be obtained by considering the reaction


(3)

To the extent that the CH and SiH bonds are transferable (quite likely here), reaction 1 measures the relative strengths of the multiple bonds. By use of MP3/6-31G*//3-21G[20] energies, reaction 3 is found to be endothermic by 24.9 kcal/mol. If additivity of correlation and polarization effects is assumed for reaction 3, the ΔE is predicted to be 23.9 kcal/mol. This is only 1.1 kcal/mol less than the ΔE from the actual calculation and provides some justification for the additivity approximation.

Recent estimates of the C=Si π bond energy range from 35 to 55 kcal/mol[21] with Davidson's value for 1,1-dimethyl-1-silaethylene being 41 kcal/mol.[22] If the C=C π bond energy is taken to be the difference between the carbon–carbon bond energies in ethane and ethylene,[23] one finds the difference in π bond energies to be about 37 kcal/mol in favor of C=C. According to Walsh,[24] the ethane and methylsilane single bond energies are the same, so that the 37 kcal/mol applies to the net C=C vs. C=Si difference as well. Combining this result with the calculated ΔE for reaction 3, we predict the Si=O bond to be about 12 kcal/mol weaker than C=O. This value might be diminished somewhat if the Si=C π bond energy were taken from $CH_2{=}SiH_2$ rather than the methylated species. The C–H bonds are about 10 kcal/mol stronger than SiH.[24] Even if the C–Si bonds in **1** and **3** are the same, the net difference between the two isomers will be ~8 kcal/mol in favor of **1**. If, as suggested by the relative bond lengths, the Si–C bonds in **1** are stronger, this difference will increase. These speculations are at least in qualitative agreement with the actual isomerization energies given in Table III.

Conclusions

These calculations suggest that the thermodynamically most stable H_4CSiO structure is methylsilanone ($CH_3SiH{=}O$). This is consistent with the recent findings of Barton and co-workers[9] and is supported by qualitative bond energy estimates. These results also suggest that the metathesis reaction (2) appears to be thermodynamically feasible.

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Registry No. 1, 88157-93-1; **2**, 43435-60-5; **3**, 88157-95-3; **4**, 88157-96-4; **5**, 88157-94-2; **6**, 88157-97-5; H_2SiO, 22755-01-7; C_2H_4, 74-85-1.

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(20) This notation indicates an MP3 calculation using the 6-31G* basis set at the 3-21G geometry.

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(22) I. M. T. Davidson, 17th Organosilicon Symposium, June 1983.

(23) See, for example, P. W. Atkins, "Physical Chemistry", W. H. Freeman and Co., San Francisco, 1982.

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(25) **Note Added in Proof**: Since acceptance of this paper, full MP3/6-31G* calculations have been carried out on three of the isomers studied here: **1**, **2**, and **3**. The results are slightly different from those obtained from the acidity assumption, since isomer **1** is now found to be 2.6 kcal/mol below **2**. Since this energy difference is less than that found for silylene vs. silaethylene at the same level of theory, it is still likely that isomer **2** will ultimately be the most stable. The energy gap between **2** and **3** increases by about 6 kcal/mol. Furthermore, it has very recently been found [T. Kudo and S. Nagase, *J. Organomet. Chem.*, **253**, C23 (1983)] that the silanone to hydroxysilylene isomerization barrier is about 60 kcal/mol. This again argues for reaction 1 not readily occurring.