corrected CISD), and 32.6 kcal (CCSD). Thus, the coupled cluster results exert only a modest correction to the CISD predictions.

As noted in Previous Theoretical Work, Jug, Dwivedi, and Chickos[24] predicted dioxetane structure **4** to lie below diketene by 12 kcal. However, since the dioxetane structure had never been observed, those authors concluded that their prediction must be incorrect. We confirm this argument of Jug, Dwivedi, and Chickos in the present research by showing that the dioxetane structure lies about 31 kcal above diketene. The second-order perturbation theory prediction (4-31G basis set) of 48.2 kcal for ΔE (1 → 4) by Fu, Decai, and Yanbo[29] appears somewhat high in this regard.

Concluding Remarks

We have reported a comprehensive theoretical study of diketene (**1**), 1,3-cyclobutanedione (**2**), and 2,4-dimethylene-1,3-dioxetane (**4**). Of these, diketene is well-characterized experimentally, and the theoretical predictions are broadly concordant. However, in light of differences between theory and the two existing experimental structures (both unfortunately dating from the 1950s), a precise modern structural study would be most welcome.

Most of the theoretical results for cyclobutanedione **2** and

dioxetane **4** structures are true predictions; i.e., there are no experiments with which to make comparison. However, this work has allowed us to assign three previously unidentified features of the infrared spectrum of 1,3-cyclobutanedione. We hope that the present theoretical predictions will stimulate new experiments on 1,3-cyclobutanedione, which is essentially degenerate with the better known diketene molecule. The dioxetane structure lies only about 32 kcal above diketene and is a genuine minimum on the DZ+P SCF potential energy hypersurface. The synthesis of the dioxetane isomer should be achievable and would be an important scientific accomplishment.

This paper has not attempted to explain the observed primary formation of diketene over 1,3-cyclobutanedione from two ketenes. The equilibrium thermodynamic results do not seem to provide any hint concerning the answer to this question. In the future we hope to carry out detailed quantum mechanical studies of the various transition states for ketene dimerization.

Registry No. 1, 674-82-8; **2,** 15506-53-3; **4,** 68498-71-5.

A Theoretical Study of the Reaction of Ground-State Silicon with Ethylene and Acetylene

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Abstract: It has recently been demonstrated by kinetic studies that the reaction of Si(^{3}P) with C_2H_4 proceeds at almost unit collisional efficiency. In this paper the corresponding potential surfaces have been examined by ab initio methodology, by using the UMP2 method with spin projection. It is found that the lowest triplet equilibrium structure is a silacyclopropylidene structure ($^3A_2$), for which there is no barrier to its formation. Fourteen other low-lying triplet structures are also reported. A similar study is also reported for Si(^{3}P) with C_2H_2.

I. Introduction

In a recent publication, Basu and Husain[1] reported absolute rate data for the reaction of ground-state atomic silicon, Si(^3P_J), with olefins determined by time-resolved atomic resonance absorption spectroscopy. In particular the decay of the ground-state Si was monitored in the presence of ethylene, for which the absolute second-order rate constant (k_R, T = 300 K) was measured as 8.8 ± 1.5 × 10^{-11} cm^3 mol^{-1} s^{-1}. This implies that the reaction proceeds at close to unit collisional efficiency. The evidence therefore is that one or more stable complexes are formed from the reaction of Si(^{3}P) with C_2H_4. Our purpose is to study the approach of Si(^{3}P) to C_2H_4, locating in particular minima and barriers in any reaction pathway. Basu and Husain refer to some earlier ab initio calculations. Barthelat, Trinquier, and Bertrand[2] performed pseudopotential SCF studies on SiC$_2$H$_4$, finding that silylacetylene, SiH$_3$—C≡CH (**14**), was the most stable singlet structure, with silacyclopropene and silacyclopropylidene, **1**, both being 17 kcal/mol higher in energy (see Figure 1). Silaallene CH$_2$=Si=CH$_2$ is much higher in energy at 46 kcal/mol, and silapropyne CH$_3$Si≡CH is 60 kcal/mol higher. Double-ζ closed shell SCF geometry optimizations were performed by Lien and Hopkinson,[3] who confirmed some of the previous findings. They

found silylacetylene to be the lowest, with silacyclopropene and silacyclopropylidene being 15.2 and 17.2 kcal higher in energy. Vinylsilylene, 3 CH$_2$=CH—SiH, and ethylidenesilylene, CH$_3$—CH=Si **6**, were also investigated and found to be 15.4 and 18.0 kcal higher in energy. They observe therefore that silacyclopropene and three divalent structures all lie within 20 kcal of the lowest state. More sophisticated calculations at the SCF level (6-31G*//3-21G) (closed shell) were carried out by Gordon and Koob,[4] who found similar results.

The situation is therefore very different to the analogous carbon structures (see Figure 3). The most detailed calculations, of relevance to this work, are by Yoshimine, Honjou, and Pacansky,[5] who report SCF and CI studies of C$_3$H$_4$. They show that the trans planar carbene **18** ($^3A''$) lies 50 kcal/mol above the almost degenerate singlet states of allene and methylacetylene, with the $^3B_1$ cyclopropylidene **15** structure lying 26 kcal/mol above the $^3A''$ **18** structure. Predominately Yoshimine et al. were concerned with singlet structures, but they state that cyclopropylidene has a singlet ground state, lying 12 kcal/mol below the $^3B_1$ **15** structure.

There are very few calculations on triplet states of SiC$_2$H$_4$. Barthelat et al.[2] report that the $^3B_1$ silacyclopropylidene (**1b**) lies 51.6 kcal/mol above the singlet silylacetylene **14**. Krogh-Jespersen[6] has performed the most accurate studies to date. In

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(2) Barthelat, J.-C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979,** *101,* 3785.

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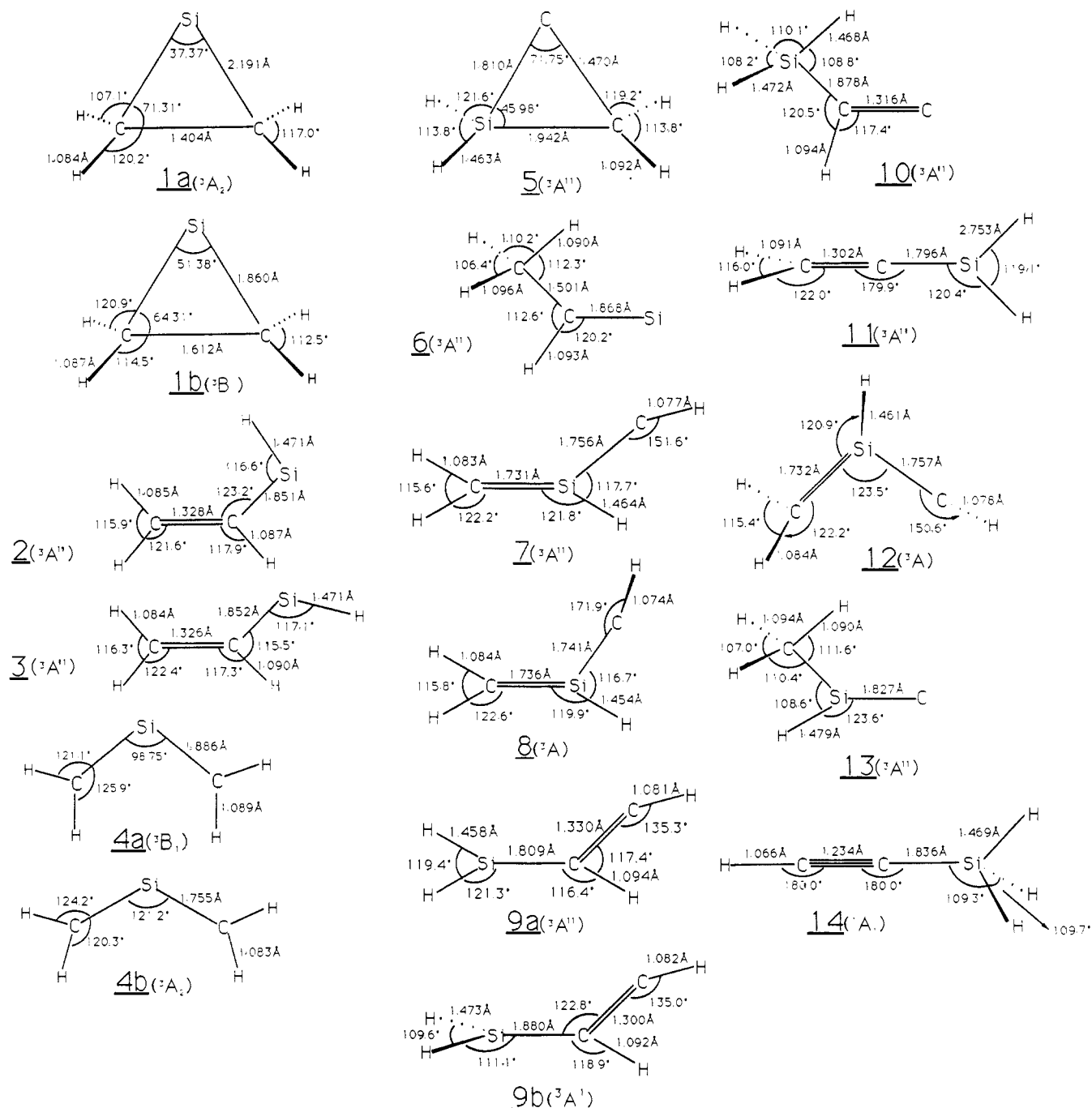(6) Krogh-Jespersen, K. *J. Comput. Chem.* **1982,** *3,* 571.

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Figure 1. Details of UMP2(DZP) optimized structures for 15 triplet isomers of SiC$_2$H$_4$, together with the MP2 (DZP) optimized singlet structure **14**.

particular the $^3A_2$ state of planar CH$_2$–Si–CH$_2$ (**4**) and the $^3A''$ state of planar SiH$_2$–C–CH$_2$ (**5**) were studied, which were found at the UMP3/6-31G* level to be 19.1 and 35.9 kcal/mol above the respective silaallene and SiH$_2$=C=CH$_2$ singlet structures. Considerable spin contamination was noticed for the $^3A_2$ structure ($\langle \hat{S}^2 \rangle$ = 2.33).

In this paper we shall investigate minima on the lowest triplet surfaces of each symmetry of SiC$_2$H$_4$. We shall also discuss the incidence of barriers in the formation of the SiC$_2$H$_4$ structures.

Basu and Husain[7] have reported similar kinetic studies of Si(^3P_J) with acetylene, with similar results. The ab initio situation on SiC$_2$H$_2$ is also similar to that for SiC$_2$H$_4$, in so far as that there are some good calculations on a variety of singlet isomers by Frenking, Remington, and Schaefer.[8] The lowest singlet structure

is silacyclopropenylidene (**24**), with vinylidenesilene (**22**) and silylenylacetylene (**16**) calculated to lie 17 and 22 kcal/mol higher in energy (see Figures 4 and 5). There appear to be no calculations on triplet states of SiC$_2$H$_2$. On the other hand, Lee, Bunge, and Schaefer[9] examined cyclopropenylidene, finding the singlet state to lie ~70 kcal/mol below two triplet states, $^3B_1$ and $^3A_2$, of nearly equal energy, although they report that the $^3A_2$ is not a minimum on the surface. However, their results disagree with earlier calculations of Hehre and Pople et al.[10] who suggest that a nearly linear propargylene is the lowest triplet state. They found that cyclopropenylidene is the lowest singlet structure. Vinylidene carbene has been observed by Maier et al.,[11] and they have

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(8) Frenking, G.; Remington, R. B.; Schaefer, H. F. J. Am. Chem. Soc. 1986, 108, 2169.

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(10) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. J. Am. Chem. Soc. 1976, 98, 4378.
(11) Maier, E.; Reisenauer, H. P.; Schwab, W.; Carsky, P.; Hess, B. A.; Schaad, L. J. J. Am. Chem. Soc. 1987, 109, 5183.

Reaction of Ground-State Si with H_2C=CH_2 and HC≡CH

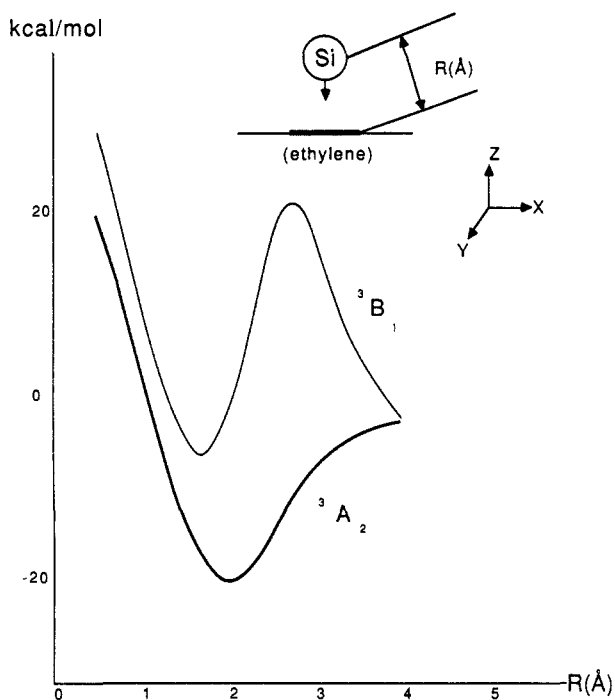*J. Am. Chem. Soc., Vol. 112, No. 4, 1990* 1501

Figure 2. The C_{2v} approach of Si(^{3}P) to C_2H_4 in (a) $^3A_2$ symmetry and (b) $^3B_1$ symmetry.
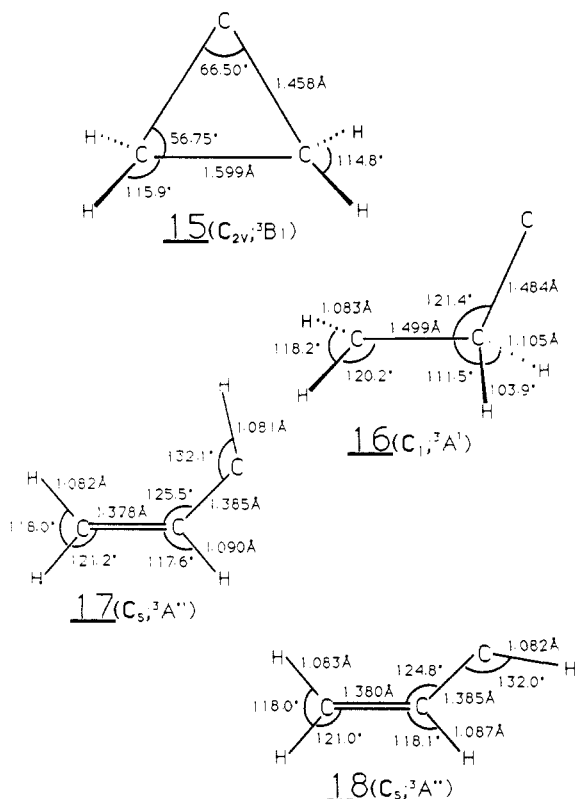

Figure 3. Selected triplet isomers **15–18** of C_3H_4, optimized at the UMP2(DZP) level.

performed calculations on the singlet and triplet states. We shall therefore also report some studies on the triplet isomers of SiC_2H_2.

II. Methodology

We have studied these systems by using a variety of ab initio quantum chemistry methods for open shell molecules. Firstly, we used both the restricted Hartree–Fock scheme (RHF) and the unrestricted Hartree–Fock scheme (UHF), which is not a spin eigenfunction, the deficiency being measured by a determination of $\langle S^2 \rangle$. To include dynamical correlation we used the unrestricted Møller–Plesset scheme at second-order (UMP2). We have shown[12] that UHF calculations for which $\langle S^2 \rangle$

differs by more than 10% from its correct value (in this case 2.0) must be viewed with caution. At the UMP2 level, it is possible to remove some of the spin contamination by a projection method.[13] In particular we have formulated[13] a scheme which removes the two (2) worst spin contaminants, and we called it PUMP2 (2). Thus we shall report calculations at the RHF, UHF, UMP2, and PUMP2 (2) level of approximation. We are also able to evaluate energy gradients at the UHF and UMP2 levels, and thus geometries have been optimized at these levels of approximation. The basis sets we have used are the usual minimal basis set STO-3G,[14] for initial investigations, and more refined calculations using double-ζ plus polarization basis sets (DZP). For carbon this consists of the Dunning[15] 4s2p contraction of Huzinaga's[16] 9s5p primitive set to which are added a d function of exponent 0.8; the p function on the hydrogen has exponent 1.0; for silicon, likewise, we used the Dunning[15] 6s4p contraction of Huzinaga's[17] 11s7p primitive set to which one adds a d function of exponent. Further calculations were also performed with a TZ2P basis set. The TZ2P basis set is defined by the triple-ζ contractions of Huzinaga primitives for Si (12s9p/9s6p)[18] and for C (10s6p/5s4p).[19] The polarization exponents were α_d(Si) = 1.86, 0.59, 0.20 and α_d(C) = 1.2, 0.4. For SiC_2H_4 and SiC_2H_2 systems this TZ2P basis set involved 139 and 121 basis functions, respectively.

All calculations were performed by using the Cambridge Analytic Derivatives Package (CADPAC).[20]

III. Triplet Structures for SiC_2H_4

The 13 triplet structures considered are depicted **1–13** in Figure 1. **1a, 1b,** and **5** may be termed cyclic structures, with **1a** and **1b** commonly referred to as silacyclopropylidene. **4** is a planar form of bent silaallene. **11** is a silaallene structure. **6, 10** and **13** are the three possible forms of ethylidenesilylene. **2, 3, 7, 8, 9,** and **12** are various forms derivable from vinylsilylene. We examined other possible structures at the RHF-STO-3G level, but only these were found to be minima on the surfaces. We then optimized the structures at both the UHF and UMP2 levels of theory with a DZP basis sets. At the UMP2 optimized geometries shown in Figure 1, PUMP2(2) calculations were then performed. The results are given in Table I. Structure **14** is the important silylacetylene singlet structure.

For the structures **1a** and **1b** of C_{2v} symmetry, combination of the π, π^* orbitals on C_2H_4 with the 3p orbitals on Si yield a_1 and b_2 bonding orbitals and the b_1 ($3p_y$) nonbonding orbitals. Thus $^3A_2$, $^3B_2$, and $^3B_1$ states may be formed. The $^3B_2$ state (...$b_1^2a_1b_2$) at the RHF-STO-3G level was found to be considerably higher than the other two states and was not considered further. The $^3A_2$ state (...$a_1^2b_1b_2$) has the doubly occupied π (a_1) orbital and thus has a much shorter CC bond than the $^3B_1$ state (...$b_2^2a_1b_1$). The $^3B_1$ state is 13 kcal/mol higher than the $^3A_2$ state. In Table I separate calculations on Si (^{3}P) and ethylene are reported, enabling us to deduce that both the $^3A_2$ and $^3B_1$ are stable with respect to dissociation. At dissociation Si + C_2H_4 may be described as ...$a_1^2b_1b_2$, and thus it is not expected that there will be a barrier to the formation of the $^3A_2$ state, whereas there will be for the $^3B_1$ state. This is clearly demonstrated in Figure 2, where the C_{2v} approach (z-axis) of Si to C_2H_4 is calculated by using the UMP2/DZP method. Within reason, this is the best that can be done today—for each value of R, the other coordinates have been optimized by using analytic gradients. It therefore appears that this $^3A_2$ (**1a**) isomer can be formed from Si(^{3}P) + C_2H_4 without a barrier.

Structures **2** and **3** are planar, and they correspond to the insertion of Si into a CH bond. The configuration is $1a''^2a'2a''$, where where $1a''$ is C=C π bonding orbital, a' is nonbonding p_x on Si and $2a''$ is nonbonding p_y on Si. It is noted from Table I

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(18) Huzinaga, S. Department of Chemistry Report, University of Alberta Edmonton, Alberta, Canada, 1971.

(19) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

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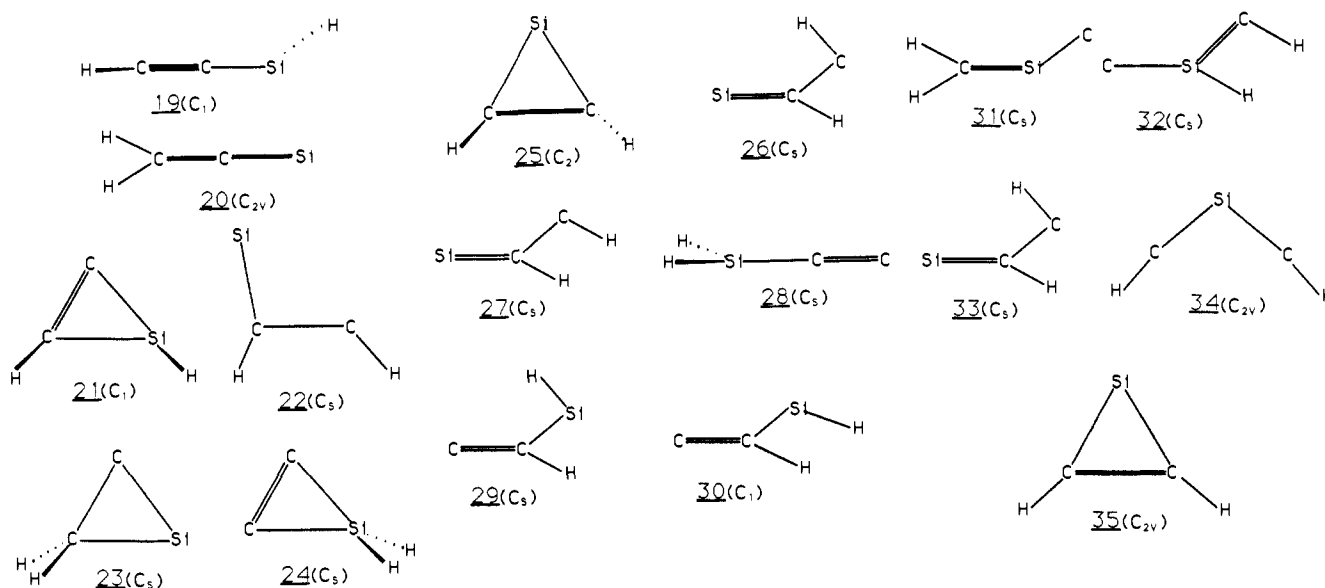
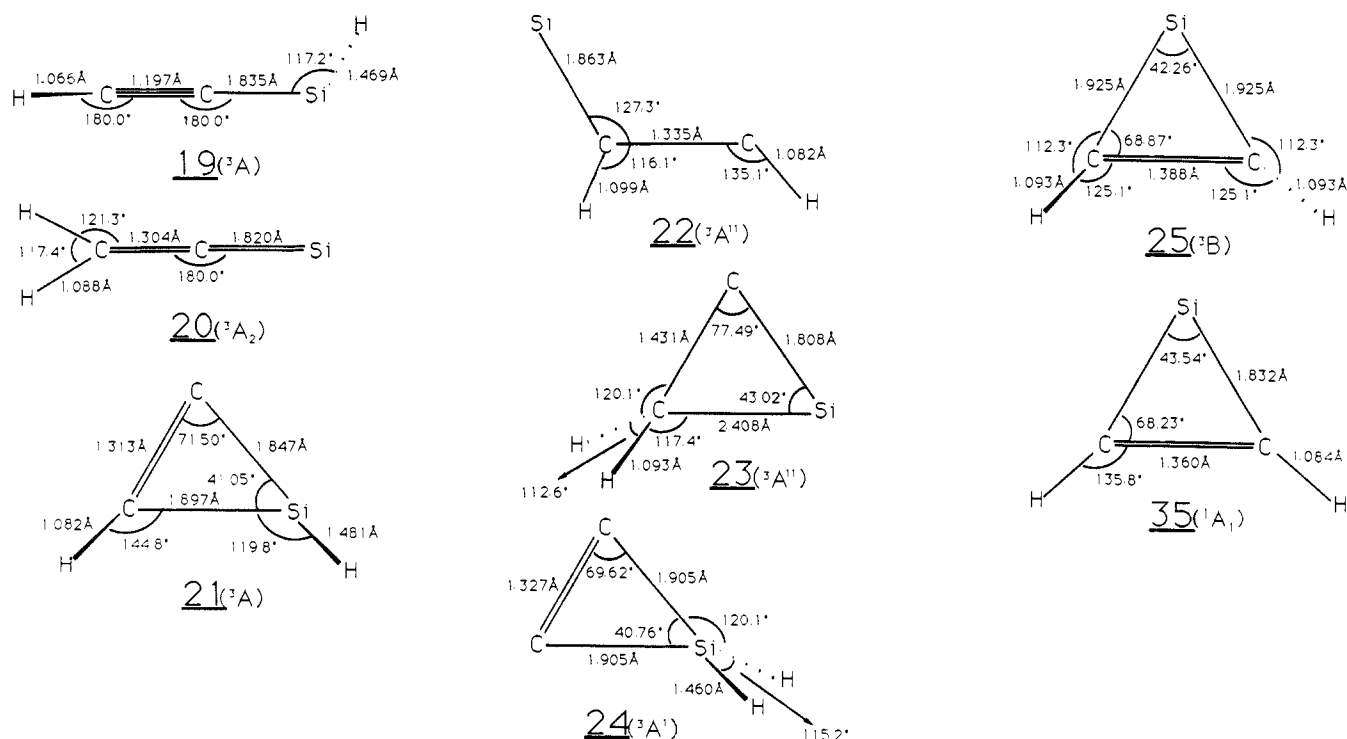Figure 4. 19–35 show the geometries of triplet isomers of SiC_2H_2.

Figure 5. Details of UMP2(DZP) optimized structures for seven triplet and one singlet isomer of SiC_2H_2.

that these vinylsilylene structures are both low-lying isomers.

Structures 4 may be considered as arising from an approach of Si to C_2H_4, in the plane of C_2H_4, perpendicular to the CC bond. The relevant orbitals are the b_2 π-bond combination on C_1SiC_2, the π-antibonding a_2 orbital on C_2C_2, and the a_1 σ-bonding combination involving orbitals on C_1, Si, and C_2. Thus we expect the $^3B_1$ (...$a_1^2b_2a_2$) and the $^3A_2$ (...$b_2^2a_2a_1$) to be the low-lying states. Table I shows that the $^3A_2$ is just bound with respect to dissociation. Because there is no a_2 orbital on Si, there will be a barrier to the formation of this $^3A_2$ state as Si approaches C_2H_4. If the b_1 nonbonding orbital of Si is also considered, then the configurations $a_1^2b_2b_1$, $^3A_2$, and $b_2^2b_1a_1$, $^3B_1$ are also found to be minima on the surface, but they have much higher energy.

Structure 5 is the analogue of structures 1a and 1b, with C and Si interchanged. The relevant orbitals are the a'' nonbonding p_x on the lone C_1, the $1a'$ bonding combination between p_y on C_1 and the antibonding $*_z$ combination of Si–C_2, and the $2a'$ combination between p_z on C_1 and the π_z bond of Si–C_2. Thus the

configuration is ...$a'^2a'a''$; it is a minimum, but as seen from Table I it is quite high in energy.

Silylidene structure 6 has a plane of symmetry; the relevant orbitals are the $1a'$ Si–C σ bonding orbital, the $2a'$ nonbonding p_z on Si, and the a'' nonbonding p_x on the central C. The configuration is ...$1a'^22a'a''$, and it is stable with respect to dissociation.

The remaining structures, 7, 8, 9a, 9b, 10, 11, 12, and 13 are all minima, but they all have energy higher than Si + C_2H_4 and are therefore of not such great interest. With the exception of 11, it is noted from Table I that they all have some spin contamination in their description. It is interesting to observe that both 7 and 8 are minimum but corresponding to a relatively free CH rotation. We investigated structure 9b commencing with a silacyclopropene structure, in view of its low-lying singlet nature. However, on optimization structure 9b was obtained, which was noticed to have about the same energy as 9a.

UMP2 optimized structures with a DZP basis are shown in Figure 1. In all these structures there is a variety of Si–C bonds

Reaction of Ground-State Si with $H_2C{=}CH_2$ *and* $HC{\equiv}CH$

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Table I. Energies of Selected Triplet Configurations for SiC_2H_4, Obtained with a DZP Basis Set

configuration	symmetry	UHF (hartree)	UMP2 (hartree)	PUMP2 (hartree)	$\langle S^2 \rangle$	ΔH (kcal/mol) PUMP2
Si	^3P	−288.832 288	−288.936 453	−288.937 156	2.006	
C_2H_4	^1A_g	−78.050 054	−78.351 857	−78.351 857	0.0	
1a	$^3A_2$	−366.887 791	−367.314 537	−367.316 615	2.036	−17.3
1b	$^3B_1$	−366.863 014	−367.295 975	−367.295 348	2.007	−3.97
2	$^3A''$	−366.902 656	−367.308 185	−367.314 908	2.148	−16.3
3	$^3A''$	−366.902 660	−367.308 085	−367.314 829	2.148	−16.2
4a	$^3B_1$	−366.873 383	−367.266 634	−367.268 544	2.018	+12.8
4b	$^3A_2$	−366.876 042	−367.281 130	−367.290 456	2.255	−0.905
5	$^3A''$	−366.842 492	−367.251 607	−367.253 745	2.025	+22.1
6	$^3A''$	−366.896 628	−367.303 708	−367.305 731	2.027	−10.5
7	$^3A''$	−366.869 857	−367.253 707	−367.266 974	2.349	+13.8
8	$^3A''$	−366.868 723	−367.252 944	−367.266 589	2.351	+14.1
9a	$^3A''$	−366.871 509	−367.261 379	−367.273 604	2.257	+9.67
9b	$^3A'$	−366.872 898	−367.267 461	−367.275 286	2.177	+8.61
10	$^3A''$	−366.835 860	−367.208 291	−367.220 842	2.339	+42.8
11	$^3A''$	−366.865 792	−367.272 236	−367.275 543	2.057	+8.45
12	^3A	−366.869 700	−367.253 875	−367.267 089	2.348	+13.8
13	$^3A''$	−366.814 542	−367.215 849	−367.216 823	2.012	+45.3
14	$^1A_1$	−366.933 960	−367.375 560	−367.375 560	0.0	−54.3

Table II. Energies of Selected Triplet Configurations for $Si(C_2H_4)$, Obtained with a TZ2P Basis Set

configuration	symmetry	UHF (hartree)	UMP2 (hartree)	PUMP2 (hartree)	$\langle S^2 \rangle$	ΔH (kcal/mol) PUMP2
Si	^3P	−288.853 317	−289.089 413	−289.090 686	2.014	
C_2H_4	^1A_g	−78.064 477	−78.427 223	−78.427 223	0.0	
SiC_2H_4						
1a	$^3A_2$	−366.923 794	−367.545 129	−367.547 896	2.047	−18.8
2	$^3A''$	−366.938 337	−367.537 026	−367.543 723	2.146	−16.2
3	$^3A''$	−366.937 888	−367.536 470	−367.543 304	2.149	−15.9

Table III. Energies of Selected Triplet Configurations for SiC_2H_2, Obtained with a DZP Basis Set

configuration	symmetry	UHF (hartree)	UMP2 (hartree)	PUMP2 (hartree)	$\langle S^2 \rangle$	ΔH (kcal/mol) PUMP2
Si	^3P	−288.832 288	−288.936 453	−288.937 156	2.006	
C_2H_2	^1A_g	−76.830 073	−77.115 507	−77.115 507	0.0	
19	^3A	−365.700 520	−366.085 027	−366.090 899	2.109	−24.0
20	$^3A_2$	−365.704 137	−366.085 857	−366.090 136	2.078	−23.5
21	^3A	−365.660 293	−366.060 711	−366.064 744	2.066	−7.58
22	$^3A''$	−365.686 221	−366.048 571	−366.060 565	2.253	−4.96
23	$^3A''$	−365.654 492	−366.047 512	−366.050 225	2.038	+1.53
24	$^3A'$	−365.611 659	−366.009 166	−366.012 421	2.040	+25.3
25	^3B	−365.644 399	−366.039 556	−366.044 112	2.091	+5.37
35	$^1A_1$	−365.745 285	−366.166 452	−366.166 452	0.0	−71.4

Table IV. Energies of Selected Triplet Configurations for $Si(C_2H_2)$, Obtained with a TZ2P Basis Set

configuration	symmetry	UHF (hartree)	UMP2 (hartree)	PUMP2 (hartree)	$\langle S^2 \rangle$	ΔH (kcal/mol) PUMP2
Si	^3P	−288.853 317	−289.089 413	−289.090 686	2.014	
C_2H_2	^1A_g	−76.845 582	−77.188 354	−77.188 354	0.0	
SiC_2H_2						
19	^3A	−365.738 092	−366.311 267	−366.317 386	2.114	−24.1
20	$^3A_2$	−365.738 804	−366.307 533	−366.313 454	2.108	−21.6

and C–C bonds, for C–C we find bond lengths varying from 1.30 (11) to 1.40 Å (1b) and for Si–C varying between 1.70 (13) and 2.19 Å (1b). Although not really appropriate, in Figure 1 we have classified C–C bonds as double bonds if they are less than 1.35 Å, and Si–C as double bonds if they are less than 1.76 Å.

Larger calculations with the TZ2P basis set were performed on the structures 1a, 2, and 3 to determine which is the lowest triplet isomer. The results are reported in Table II. It is seen that the $^3A_2$ structure, 1a, remains the most stable isomer. In order to put these calculations in context, the ground state (singlet) of SiC_2H_4, silylacetylene (14), was also optimized with the DZP basis set. It is seen from Table I that the lowest triplet 1a lies 37 kcal/mol higher in energy than 14.

The situation is to be contrasted with C_3H_4. The calculations of Yoshimine et al.[5] show that the $^3A''$ trans planar carbene 18 lies 50.5 kcal/mol above the ground $^1A_1$ methylacetylene (using a CI calculation in a DZP basis). The two vinylmethylenes 17 and 18 are almost degenerate. The $^3B_1$ cyclopropylidene 15 lies

25.4 kcal/mol above the $^3A''$ carbene 18 (in contrast with SiC_2H_4 where the $^3B_1$ 1b lies about 12 kcal/mol above the $^3A''$ 3). Figure 3 shows the relevant UMP2-DZP structures of C_3H_4 for this discussion. The energy order of these four selected isomers is 18 (0 kcal/mol) < 17 (0.05 kcal/mol) < 15 (29.5 kcal/mol) < 16 (73.5 kcal/mol) at the UMP2(DZP) level. This order is the same as in Yoshimine et al.[5] However, they did not consider the $^3A_2$ cyclopropylidene (15); with a minimum basis we find that this $^3A_2$ state lies 55 kcal/mol above the $^3B_1$. As with SiC_2H_4, the $^3A_2$ has one imaginary frequency at this low level of calculation. On optimization to the $^3A'$ structure 16, it is still 44 kcal/mol above the $^3B_1$ at the UMP2(DZP) level. It therefore seems most unlikely that the $^3A'$ (or $^3A_2$) structure will be a low lying isomer of C_3H_4, in contrast to the SiC_2H_4 situation.

IV. Triplet Isomers of SiC_2H_2

In Figure 4 are shown 16 structures all of which were minima when optimized at the RHF-STO-3G level. Hehre et al.,[10] when

considering the triplet structures of C_3H_2, found that the lowest was propargylene ($\sim$19), followed by propadienylidene ($\sim$20), propenediylidene ($\sim$22, $\sim$26), cyclopropenylidene ($\sim$21, $\sim$25), and cyclopropyne ($\sim$23, $\sim$24). Our calculations at the minimal level suggest that the lowest triplet structures are **19–25** and that these were then optimized at the UMP2(DZP) level, and results are given in Table III.

These calculations show that the Si insertion structure **19** (^3A) is the lowest, with the structure **20** ($^3A_2$) lying very close in energy. As shown in Tables III and IV, the energy difference between them is 0.5 and 2.5 kcal/mol at the UMP2(DZP) and UMP2-(TZ2P) levels, respectively. **19** does not have the odd W shaped structure proposed by Hehre et al. for C_3H_2 but seems to be an entirely reasonable structure for the Si-containing molecule. The structure for **20** is again acceptable and favorable because it can be drawn with a C=Si bond.

If one considers a C_{2v} approach of Si(^3P) to C_2H_2, then in analogy with SiC_2H_4 there will be $^3B_1$, $^3B_2$, and $^3A_2$, which is found again to have one imaginary frequency. On distortion the low-lying structure $^3A''$ **22** is found which can be formed from Si(^3P) and C_2H_2 without a barrier. In this case the $^3B_1$ is not a minimum, but the optimized structure **25**, ^3B, is a minimum.

Structure **23** is considerably lower in energy than structure **24**, corresponding again to Si's preference for divalency.

We believe that structures **19–25** include the lowest triplet structure of SiC_2H_2. The lowest singlet is the silacycloprope-

nylidene structure, as determined by Frenking et al. from an examination of 15 isomers. We optimized this structure, and it is shown in Figure 5 as structure **35**; its energy is reported in Table III from which it is seen that it lies 47 kcal/mol below the lowest triplet isomers **19** and **20**.

V. Conclusion

In this paper we have studied the triplet isomers of SiC_2H_4 and SiC_2H_2. Our results may be summarized as follows.

(i) The lowest energy structure of SiC_2H_4 is the $^3A_2$ structure **1a** of Figure 1. It may be formed from Si (^3P) + C_2H_4 without a barrier. There are two other structures, **2** and **3**, which lie close in energy to **1a**. Structure **1a** lies 37.0 kcal/mol above the global minimum singlet structure **14** (Figure 1).

(ii) The lowest energy structure of SiC_2H_2 is the ^3A structure **19** with the $^3A_2$ structure **20** having almost the same energy, both lying 48 kcal/mol above the global minimum singlet structure **35**. The structure **22** which is bound with respect to Si(^3P) + C_2H_2 may be formed without a barrier. Note that this is not a ring structure (unlike the $^3A_2$ structure **1a** in Si(^3P) + C_2H_4).

Finally therefore, the kinetic experiments of Basu and Husain may be explained: for Si(^3P) + C_2H_4, the low-lying structure **1a** is formed without a barrier; for Si(^3P) + C_2H_2, the structure **22** of may be formed without a barrier, although in this case it is not the lowest triplet structure.

Tautomerism of 2- and 4-Thiouracil. Ab Initio Theoretical Study

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Abstract: Ab initio quantum mechanical studies on tautomerism are extended to the 2-thiouracil and 4-thiouracil molecules. We considered the protomeric tautomerism in vacuum and conclude that for both species the oxo–thione forms should prevail in full agreement with recent experimental matrix isolation studies. Surprisingly, the next most stable structure appears to be the hydroxy–mercapto form. The relevance of the relative stability order of 2-thiouracil and 4-thiouracil to the tautomerism of various derivatives is discussed. Major features of the vibrational spectra of various tautomeric forms are presented and compared with the experiment.

The protomeric tautomerism of heterocycles, including biologically important pyrimidines and purines, has attracted considerable attention for almost half a century.[1] Both experimental[1,2] and theoretical[2,3] efforts were directed toward determination of numerous physicochemical properties of possible tautomeric forms. It has been realized that the relative population of these forms strongly depends on the environment.[3,4] In particular, the form dominating in the gas phase or in the nonpolar solvents may completely disappear in the crystalline state or in the polar solvents and may be replaced by another tautomeric form. Such a dramatic shift in concentrations will certainly affect the metabolism of heterocycles in biological systems. In the context of our theoretical studies on the tautomerization phenomenon, we have recently directed our interest toward the tautomerism of nucleobase thio derivatives that contain sulfur atoms in the positions of the exocyclic oxygen atoms. Their protomeric tautomerism is somewhat different than that of the parent bases.[5] The thiated nucleobases appear naturally in various

biological materials and are important agents for numerous metabolic processes. Many of them have been characterized in tRNAs,[6] e.g. 4-thiouridine in prokaryotic tRNAs, 2-thiouridine in Drosophila tRNA^{Glu},[7] and 2-thiocytidine in prokaryotic tRNA.[6] Also, the corresponding thio derivatives of the purinic base have been identified.[8] It is reasonable to assume that in some nucleic acids the sulfur substitution affects the conformations of a helix

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