



ELSEVIER

5 August 1994

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 225 (1994) 410–415

An ab initio molecular orbital study of $\text{SiH}_2 + \text{F}_2 \rightarrow \text{SiH}_2\text{F}_2$

Philippe Y. Ayala, H. Bernhard Schlegel

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

Received 5 April 1994; in final form 6 June 1994

Abstract

The insertion of SiH_2 into F_2 has been studied with MP2, CCD, CISD and QCISD. For fluorine approaching syn to the silicon lone pair, the complex is 2.5 kcal/mol below reactants and the insertion barrier is 0.5 kcal/mol above reactants at QCISD/6-31G*; for the anti approach, there is no barrier (only a broad plateau) and insertion proceeds with inversion at silicon. With RQCISD, both pathways go directly to SiH_2F_2 , but with RMP2 and RCCD, there are several structures in the $\text{SiH}_2\text{F}-\text{F}$ region of the surface that are artifacts of the level of theory.

1. Introduction

Silylene is quite reactive and readily inserts into a wide variety of bonds [1]. The reverse reaction, 1,1 elimination to form a silylene, is the dominant pathway for thermal decomposition of silanes. Silylene and silylene-like surface defects may also be important in chemical vapor deposition [2] and etching [3] at silicon surfaces. Consequently, the reactions of silylene have received considerable attention, both experimentally [1–3] and theoretically¹.

The insertion of SiH_2 into F_2 is a special case because of the strength of the Si–F bond and the weakness of the F–F bond. This reaction may also be relevant to the etching of silicon surfaces by F_2 [3,5]. Our earlier calculations [6] showed that SiH_2 and F_2 approach each other along a non-least motion path with the fluorine either syn or anti to the silylene lone pair. These calculations also showed that a higher level of theory was needed to describe the potential energy surface of this reaction properly. In this Letter, we

report the results of MP2, CCD, CISD and QCISD calculations on the transition states and reaction paths for $\text{SiH}_2 + \text{F}_2 \rightarrow \text{SiH}_2\text{F}_2$.

2. Method

Ab initio molecular orbital calculations were carried out with the Gaussian series of programs [7] using the 6-31G* basis set [8]. Unless otherwise stated, all calculations are closed shell and spin restricted. Geometries were fully optimized at the MP2 [9], CCD [10], CISD and QCISD [11] levels of theory using analytical gradients. Reaction paths were followed in internal coordinates [12] and each stationary point of the MP2 potential energy surface was characterized by vibrational analysis using analytical second derivatives [13].

3. Results and discussion

Two pathways exist for the insertion of SiH_2 into F_2 . The fluorine molecule can approach either in a

¹ For recent reviews of theoretical work on silicon compounds, see Ref. [4].

syn or an anti conformation with respect to the SiH_2 lone pair. Once bonding is initiated between one fluorine and the empty SiH_2 p orbital, the remaining fluorine migrates to the SiH_2 lone pair. For the anti mechanism this migration is accompanied by the inversion of the newly formed SiH_2F center. The optimized structures for each path as well as the reactants, **1**, and product, **2**, are shown in Fig. 1. The total and relative energies of the structures are listed in Table 1. The connectivity of the various stationary points (as established by optimization or reaction path following) is illustrated in Fig. 2.

Syn pathway. Our earlier Hartree–Fock calculations [6] yielded a long-range $\text{SiH}_2\text{--F}_2$ cluster, **4**, and a transition state, **TS 5**, for the formation of the Si–F bond and migration of the fluorine to the silylene lone pair. Similar structures are found at all levels of electron correlation considered in the present work. In the cluster, the Si–F bond length is reduced by 0.570, 0.341, 0.373, 0.400 Å at the MP2, CCD, CISD, QCISD levels with respect to the HF optimized geometry. The F–F bond length in the cluster is very similar to the equilibrium F_2 bond length at the corresponding level, thus indicating that the migration has not been initiated. This cluster is found consistently at ≈ 2.5 kcal/mol lower than the reactants, except at MP2 where the well depth is 3.55 kcal/mol. In the transition state, the Si–F bond length is too short at the Hartree–Fock level, but is ≈ 2.0 Å once electron correlation is included. At correlated levels, the F–F bond shows a shortening of up to 0.05 Å compared to Hartree–Fock optimized transition structure. The overall barrier for the syn insertion is 26.17 kcal/mol at the Hartree–Fock level. The energy of the transition state relative to the reactants is much lower when electron correlation is included: –1.5, 4.53 and 5.71 kcal/mol at the MP2, CCD and CISD levels, finally becoming close to zero at the highest level of theory used in the present work (0.50 kcal/mol at QCISD). Increasing the size of the basis set may lower the relative energy of the transition state further.

The MP2 and CCD optimized geometries differ from the others by the fact that they are distorted from C_s geometry. This distortion is very small for the cluster, **4**, but in the transition state, **TS 5**, the Si–H bonds differ by 0.02 Å at the MP2 level. In contrast to the Hartree–Fock surface, reaction path following

on the MP2 surface shows that **TS 5** does not lead to SiH_2F_2 but instead heads toward $\text{SiH}_2\text{F} + \text{F}$ (structure **3**). Similar behavior can be expected on the CCD surface. Gradient following on the QCISD surface starting from **TS 5** does not show any evidence this path; instead, optimizations leads directly to SiH_2F_2 .

The MP2 and CCD surfaces show an additional artifact, transition structure **TS 6** connecting SiH_2F_2 and $\text{SiH}_2\text{F} + \text{F}$. This structure is very similar to **3** and is 33.11 and 55.06 kcal/mol above the latter at the RMP2 and RCCD levels, respectively.

Anti pathway. A long-range cluster, **7**, followed by an insertion transition state, **TS 8**, are also found on the anti pathway at the Hartree–Fock level [6]. The Si–F and F–F bond lengths in these structures are very similar to the syn analogs. The cluster well-depths are also similar (–0.95 kcal/mol for **4** and –1.01 kcal/mol for **7** at the Hartree–Fock level), but the anti barrier is 15.11 kcal/mol lower than the syn at the Hartree–Fock level. This can be attributed to an unfavorable interaction between the F–F sigma bond and the silylene lone pair in the syn conformation. Structures **7** and **TS 8** were also found at the CISD level but could not be located on either the MP2 or QCISD potential energy surfaces. Similar to the CISD calculations on **4**, the Si–F bond in **7** is 2.532 Å, the F–F bond is 1.402 Å and the well depth is –2.67 kcal/mol. Analogous to the Hartree–Fock level, the CISD calculations on **TS 5** and **TS 8** differ significantly: the Si–F bond is 0.242 Å longer, the F–F bond is 0.087 Å shorter and the Si–F–F and H–Si–F bond angles are 14.7° and 8.2° wider. The difference in the H–Si–F angle foreshadows the inversion that must take place at silicon to complete the fluorine migration. At the CISD level, **7** and **TS 8** are separated by only 0.36 kcal/mol. The QCISD potential energy surface has neither an intermediate or a transition state in this area, but only a plateau at about –2.9 kcal/mol below reactants. Beyond this plateau the optimization falls toward the product. Reaction path following on the MP2 surface leads to a stable intermediate, **9**, that is analogous to structure **3** and 6.93 kcal/mol higher than **3**. Structure **9** is accompanied by a first order saddle point, **TS 10**, that is 13.48 kcal/mol above **9** and leads to SiH_2F_2 . Similar structures are found at the CCD level, but **9** and **TS 10** do not exist on the QCISD surface.

Except for SiH_2F_2 and SiH_2F , every structure in Fig.

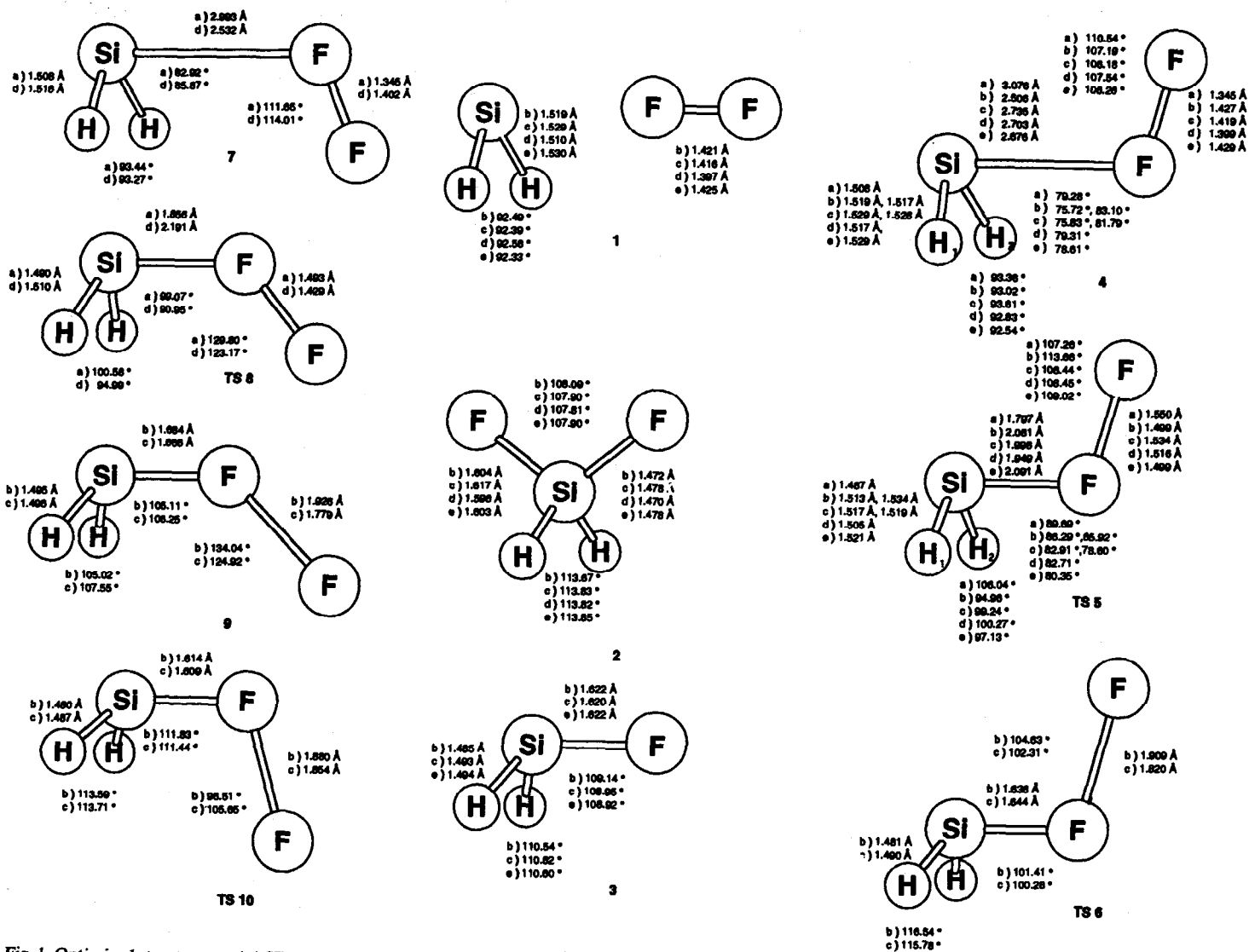


Fig. 1. Optimized structures at (a) HF, (b) MP2, (c) CCD, (d) CISD and (e) QCISD with the 6-31G* basis set. For the connectivity between the structures, see Fig. 2.

Table 1
Total energies and relative energies for $\text{SiH}_2 + \text{F}_2 \rightarrow \text{SiH}_2\text{F}_2$ ^a

Structure	HF/6-31G*	MP2/6-31G*	CCD/6-31G*	CISD/6-31G*	QCISD/6-31G*
$\text{SiH}_2 + \text{F}_2$ (1)	-488.67754 (0.00)	-489.11605 (0.00)	-489.12755 (0.00)	-489.09395 (0.00)	-489.14740 (0.00)
SiH_2F_2 (2)	-489.08181 (-253.68)	-489.52192 (-254.69)	-489.51545 (-243.41)	-489.53674 (-244.32)	-489.53674 (-244.32)
$\text{SiH}_2\text{F} + \text{F}$ (3)	-489.88779 (-131.93)	-489.26348 (-92.52)	-489.27224 (-90.79)	-489.29099 (-90.11)	-489.29099 (-90.11)
4	-488.67905 (-0.95)	-489.12171 (-3.55)	-489.13116 (-2.26)	-489.09765 (-2.32)	-489.151688 (-2.68)
TS 5	-488.63584 (26.17)	-489.11859 (-1.59)	-489.12032 (4.53)	-489.08485 (5.71)	-489.146600 (0.50)
TS 6		-489.21073 (-59.41)	-489.18450 (-35.73)		
7	-488.67915 (-1.01)			-489.09820 (-2.67)	
TS 8	-488.65992 (11.06)			-489.09763 (-2.31)	
9		-489.25244 (-85.59)	-489.21141 (-52.62)		
TS 10		-489.23096 (-72.11)	-489.20454 (-48.31)		

^a Total energies in au, relative energies (in parentheses) in kcal/mol without zero-point energy correction.

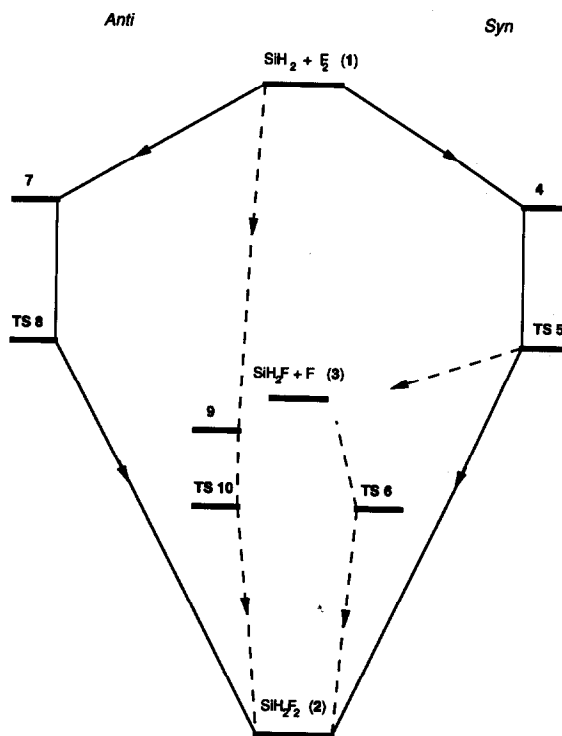


Fig. 2. Connectivity between various stationary points for $\text{SiH}_2 + \text{F}_2 \rightarrow \text{SiH}_2\text{F}_2$. The dashed lines connect MP2 and CCD stationary points, the plain lines connect HF, CISD, QCISD stationary points. Structures 7 and TS 8 do not exist at the QCISD level, this region is characterized by a plateau instead. At the MP2 and CCD level 7 and TS 8 do not exist either and the reaction path goes directly to 9. Structures 4 and TS 5 exist at the MP2 and CCD level however, the reaction path leads to 3 rather than to product.

1 suffers from RHF/UHF instability. This instability can be attributed to the spin-restricted treatment of the F-F bond. Molecular fluorine is RHF/UHF unstable at its equilibrium bond length. Since the fluorine bond is perturbed only a little in structures 4, 7, TS 5 and TS 8, the instability of these structures due to F_2 . For F_2 near its equilibrium bond length, the lowest eigenvalue of the orbital rotation Hessian of the RHF wavefunction is -0.106 and the expectation value of S^2 for the UHF wavefunction is 0.385 . This type of SCF instability can be handled reasonably well by spin-projected UMP n methods [14], and by spin-restricted methods such as RCISD, RCCSD and RQCISD that include single excitations iteratively [14]. After annihilation of the triplet spin component, the PMP2 energy is only 3.05 kcal/mol

above the RMP2 value, whereas the unprojected UMP2 energy is 24.11 kcal/mol above. The value of S^2 for the UQCISD wavefunction is 0.043 and the energy is only 0.31 kcal/mol below the RQCISD value. This good behavior of the QCISD level is further confirmed by the fact that the RQCISD and UQCISD energies of **4** and **TS 5**, differ by only 0.52 and 1.31 kcal/mol, respectively (at the RQCISD optimized geometry). Thus, the RQCISD description of the energetics for $\text{SiH}_2 + \text{F}_2$ should be reliable within the traditional margin of error of this method.

As the reaction proceeds beyond **TS 5** or **TS 8**, the F–F distance increases and Si–F bonds are formed. The quality of single reference, spin-restricted wavefunctions is expected to deteriorate rapidly and the spin-unrestricted methods are expected to be contaminated by several spin states, particularly if a stepwise, diradicaloid mechanism $\text{SiH}_2 + \text{F}_2 \rightarrow \text{SiH}_2\text{F} + \text{F} \rightarrow \text{SiH}_2\text{F}_2$ is involved. For molecular fluorine at a bond length of 1.9 Å (similar to the F–F distance in **TS 6** and **TS 10**), S^2 is 0.938 for the UHF solution the RMP2 energy is 9.47 kcal/mol higher than the PMP2 energy, indicating that the RMP2 solution is no longer reliable. For QCISD, both S^2 and the energy difference between the spin-restricted and unrestricted solutions are significantly smaller (0.653 and 5.49 kcal/mol, respectively). Since **TS 6** and **TS 10** are not found on the QCISD surface, they are most likely artifacts of the RMP2 approach.

4. Conclusions

Both the syn and the anti pathways for the insertion of SiH_2 into F_2 have been explored. A small barrier early along the reaction path is found for the syn approach. At the highest level of theory used in the present work (QCISD), there is no barrier for the anti approach. Calculations at the MP2 and CCD level find a number of additional structures in the diradicaloid ($\text{SiH}_2\text{F}-\text{F}$) part of the potential energy surfaces (**9**, **TS 6** and **TS 10**). These structures are not found on either the CISD or the QCISD surfaces and are most probably artifacts of the RMP2 and RCCD methods. At the QCISD level, optimizations started in the vicinity of **9**, **TS 6** and **TS 10** proceed directly to products. In these regions of the surface, single ex-

citations are quite important in describing the energetics of structures with elongated bonds (e.g. $\sigma \rightarrow \sigma^*$ excitations). Single excitations are absent MP2 and CCD and can result in artificial stationary points in diradicaloid regions. Single excitations are treated fairly well in the CISD and QCISD methods. Inclusion of triple excitations (e.g. QCISD(T) or CCSD(T)) may improve the description of the potential energy surface, but more extensive involvement of excited configurations would be best to treat by multireference methods.

Acknowledgement

This work was supported by a grant from the National Science Foundation (CHE 90-20398). We would like to thank the Pittsburgh Supercomputing Center and Cray Research for their generous allocations of computer time.

References

- [1] P.P. Gaspar, *React. Intermed.* 1 (1978) 229; 2 (1981) 335; 3 (1985) 333; S. Patai and Z. Rappoport, *The chemistry of organic silicon compounds* (Wiley, New York, 1989).
- [2] J.M. Jasinski and S.M. Gates, *Accounts Chem. Res.* 24 (1991) 9; J.M. Jasinski, B.S. Meyerson and B.A. Scott, *Ann. Rev. Phys. Chem.* 38 (1987) 109; K.F. Jensen, *Advan. Chem. Ser.* 221 (1989) 199.
- [3] H.F. Winters and J.W. Coburn, *Surface Sci. Rept.* 14 (1992) 165.
- [4] M.S. Gordon, J.S. Francisco and H.B. Schlegel, *Advan. Silicon Chem.* 2 (1993) 137; Y. Apeloig, *The chemistry of organic silicon compounds*, eds. S. Patai and Z. Rappoport (Wiley, New York, 1989).
- [5] P.C. Weakliem and E.A. Carter, *J. Chem. Phys.* 98 (1993) 737.
- [6] E.W. Ignacio and H.B. Schlegel, *J. Phys. Chem.* 96 (1992) 1620.
- [7] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN 92* (Gaussian, Inc., Pittsburgh PA, 1992).
- [8] P.C. Hariharan and J.A. Pople, *Theoret. Chim. Acta* 28 (1973) 213, and references therein.
- [9] C. Møller and M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [10] R.J. Bartlett, *Ann. Rev. Phys. Chem.* 32 (1981) 359.

- [11] J.A. Pople, M. Head-Gordon and K. Raghavachari, *J. Chem. Phys.* 87 (1987) 5968.
- [12] C. Gonzalez and H.B. Schlegel, *J. Chem. Phys.* 90 (1989) 2154; *J. Phys. Chem.* 94 (1990) 5523.
- [13] G.W. Trucks, M.J. Frisch, M. Head-Gordon, J.L. Andres, H.B. Schlegel and E.A. Salter, in preparation.
- [14] W. Chen and H.B. Schlegel, *J. Chem. Phys.*, in press.