Theoretical Study of Reaction Pathways for F⁻ + H₃SiCHO

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Abstract: The potential surface for the system F⁻ + H₃SiCHO has been studied using a 6-31++G** basis. Complete geometry optimizations using analytical gradients have been carried through for all species involved. All stationary points have been characterized by analytically calculated force constant matrices using the same basis. Energies were calculated at the MP4(SDTQ)/6-31++G**//RHF/6-31++G** level. Relative energies have been corrected for differences in ZPE. The initially formed adduct (FH₃Si–CHO)⁻ is found to have an energy of –50.5 kcal/mol relative to the reactants and is formed without a barrier from F⁻ and formylsilane. The axial form of the adduct is predicted to be energetically favored by 9.8 kcal/mol relative to the equatorial isomers. The reaction energy for the displacement reaction with CHO⁻ as the leaving group is found to be +6.3 kcal/mol, i.e. an endothermic reaction. Among the many subsequent reaction products obtained after rearrangement of the initially formed adduct we mention the following low-energy species: the ether (HFSi–O–CH₃)⁻ having a relative energy of –71.7 kcal/mol, and two forms of the cyclic anion (FH₂Si–CH₂–O)⁻ having the relative energies –60.3 and –61.3 kcal/mol. The highest reaction barriers predicted are associated with H-migration from Si to C in the initially formed adduct (23.9 kcal/mol) and the H-migration from Si to O in the alkoxide leading to the alcohol (H₂FSi–CH₂–OH)⁻ (23.3 kcal/mol). It has been found that the association of CH₂O and SiFH₂⁻ yielding the alkoxide (H₂FSi–CH₂–O)⁻ probably occurs without an energy barrier. The Brook rearrangement, implying a migration of a Si moiety from carbon to oxygen, has been proposed for solution reactions. The present calculations are unable to confirm such an arrangement in the gas phase.

Introduction

Acylsilanes having the general formula R₃SiCOR constitute an interesting class of chemical compounds. They are sensitive to light and rather unstable, particularly in a basic environment, where they react to give aldehydes and more complex rearrangement products.[1] Furthermore, their electronic and vibrational spectra display some unusual features.[1a,2] Since the first synthesis of a representative of this class of compounds, benzoyltriphenylsilane, by Brook et al.,[1a] a series of acylsilanes have been synthesized, isolated, and characterized, as described in reviews.[3]

A typical feature of the vibrational spectra of acylsilanes is a significant lowering of the carbonyl stretching absorption frequency as compared to the corresponding ketones. This frequency shift has been interpreted in terms of an inductive effect caused by release of electrons from the silicon atom.[3c] Also in the UV region significant shifts in spectral transitions are observed. The n → π* absorption bands for acylsilanes are located at around 370–420 nm,[2a,3a,c] which implies a shift of approximately 100 nm to longer wavelengths as compared to the carbon analogues. This suggests that acylsilanes may easily undergo photochemical reactions.

Proton resonance spectra indicate that protons attached to the α-carbon in acylsilanes are deshielded relative to their carbon analogues, and observed ¹³C signals are significantly shifted downfield as compared to the corresponding ketones.[2b,4] Experimental structural data[6] for the solid acetyltriphenylsilane, obtained by X-ray crystallography, show that the Si–CO (acetyl) bond length is 1.926 Å, *i.e.* significantly longer than a normal

Si–C single bond length which is 1.84–1.87 Å. However, the C–O bond length in the carbonyl group was found to be 1.21 Å, *i.e.* roughly the same as in a ketone, in spite of its significantly lowered vibrational frequency.

The enhanced reactivity of substituents attached to the carbon atom in the α-position to silicon is well-documented and so is the fact that functional groups located in the α-position to silicon display enhanced reactivity. This is referred to as the α-silicon effect.[1a,7]

Acylsilanes undergo a series of interesting chemical reactions that have also been utilized extensively in synthetic work.[3] Early on it was discovered that benzoyltriphenylsilane was decomposed at room temperature by dilute aqueous alcoholic alkali into triphenylsilanol and benzaldehyde.[8] This reaction cuold readily be explained in terms of nucleophilic attack on silicon by OH⁻ followed by elimination of benzoyl anion and subsequent protonation to benzaldehyde, *i.e.* as an S_N2 displacement reaction. However, a more complicated mechanism initiated by nucleophilic attack on the carbonyl carbon and subsequent rearrangements was also considered possible. By using ethoxide ion as the nucleophile Brook and Schwartz[8] found reaction products that indicated an initial nucleophilic attack on silicon followed by rearrangements.

Nucleophilic substitution at the silicon atom is of particular interest in this type of reaction as the silicon atom, in contrast to carbon, may form stable pentacoordinated compounds. For these kinetics, which may be used for synthesis of ketones and alcohols, there are thus a number of different possible reaction mechanisms:

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(1) (a) Brook, A. G.; Mauris, R. J. *J. Am. Chem. Soc.* **1957**, *79*, 971. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(2) (a) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102. (b) Brook, A. G.; Peddle, G. J. D. *Can. J. Chem.* **1963**, *41*, 2351.

(3) (a) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. (b) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (c) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 96.

(4) (a) Page, P. C. B.; Rosenthal, S. *Tetrahedron* **1990**, *46*, 2573. (b) Zweifel, G.; Miller, J. A. *Synthesis* **1981**, 288. (c) Heathcock, C.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330. (d) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. *Tetrahedron* **1983**, *39*, 949. (e) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119.

(5) (a) Bernardi, F.; Lunazzi, L.; Ricci, A.; Seconi, G.; Tonachini, G. *Tetrahedron* **1986**, *42*, 3607. (b) Olah, G. A.; Berrier, A. L.; Field, L. D.; suruya Prakash, G. K. *J. Am. Chem. Soc.* **1982**, *104*, 1349.

(6) Chieh, P. C.; Trotter, J. *J. Chem. Soc.* **1969**, 1778.

(7) (a) Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481. (b) Brook, A. G.; Gilman, H. *J. Am. Chem. Soc.* **1955**, *77*, 2322, 4827.

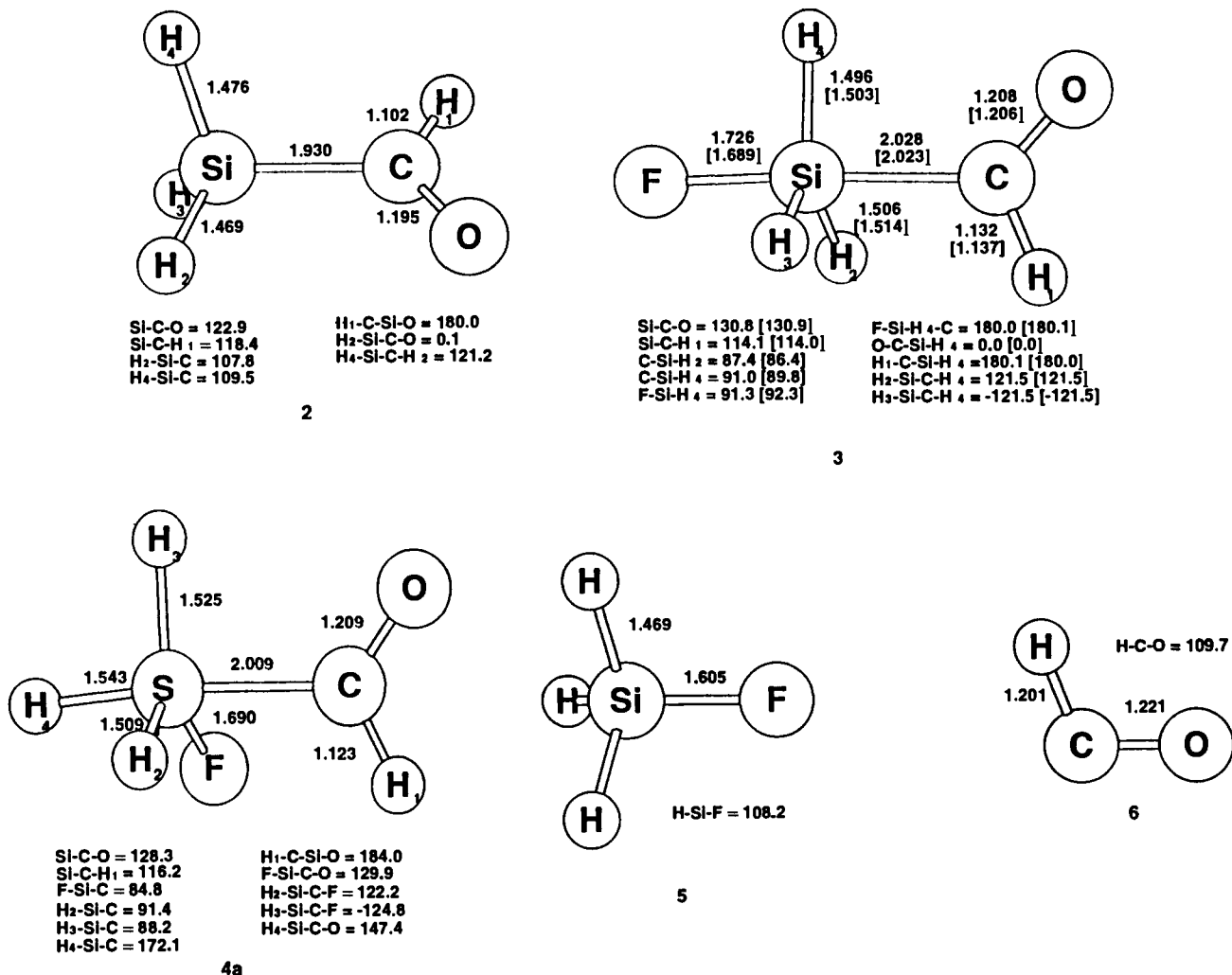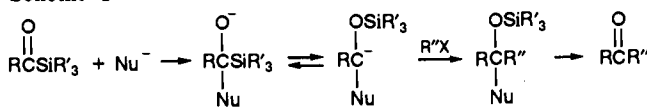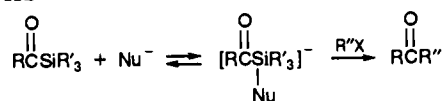(8) Brook, A. G.; Schwartz, N. V. *J. Org. Chem.* **1962**, *27*, 2311.

Figure 1. Optimized geometries at HF/6-31++G**. The minus signs on anions **3**, **4a**, and **6** have been omitted. Values in brackets on **3** are obtained using a 6-31G** basis.
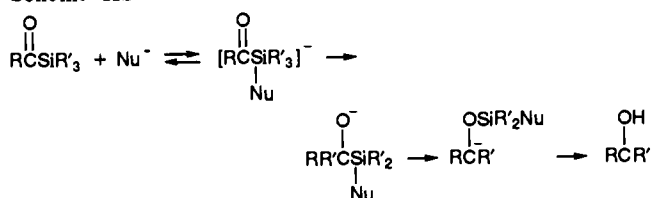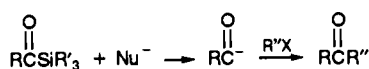
Scheme I

In Scheme I there is an initial nucleophilic attack on the carbonyl carbon, followed by a migration of the silyl group from carbon to oxygen, a so-called Brook rearrangement, and a protonation or alkylation of the resulting acyl anion and a decomposition of the resulting ether. This mechanism was suggested by Brook and Schwartz.[8]

Scheme IIa

Scheme IIb

Scheme III

In Scheme IIa there is an initial attack by the nucleophile at the silicon atom, resulting in a pentacoordinated arrangement around this atom. The resulting weakened carbon–silicon bond could then be ruptured by an appropriate electrophilic agent leading to the ketone. An alternative pathway, denoted in Scheme IIb, implies a migration of an alkyl group from silicon to carbon prior to the Brook rearrangement. Migrations of alkyl groups from silicon to carbon have been invoked in reactions leading to alcohols[9] and have also been used to account for products obtained from reactions between acylsilanes and alkoxides.[1b,8,10]

In Scheme III, also suggested by Brook and Schwartz,[8] there is a direct displacement of an acyl anion. This mechanism also opens the possibility of a decomposition of an initially formed pentacoordinated silicon atom according to Scheme II. It has been shown that desilylation of acylsilanes to give aldehydes and ketones is catalyzed by the fluoride anion.[9,11] Provided that the acyl substituent is electron withdrawing, the acyl anion may be trapped by suitable electrophiles according to Scheme III where the acylsilane acts as an acyl anion precursor. This reaction may compete with the rearrangement reaction given by Scheme IIb.

Several pentacoordinate silicon anions have been detected and studied in the gas phase,[12] using the flowing afterglow[13] and ion cyclotron resonance[14] techniques. Gas-phase experiments of this

(9) Page, P. C. B.; Rosenthal, S. *J. Chem. Res.* **1990**, 302.

(10) Brook, A. G.; Limburg, W.; Vandersar, T. S. D. *Can. J. Chem.* **1978**, *56*, 2758.

(11) (a) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201. (b) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881. (c) Page, P. C. B.; Rosenthal, S.; Williams, R. V. *Tetrahedron Lett.* **1987**, *28*, 4455.

Scheme IV

kind are very important as a reference for theoretical studies of ion stabilities and reactivities. Furthermore, accurate ab initio calculations may contribute by suggesting new species that could be looked for in gas-phase investigations under low pressure where solvent effects are absent. In a recent combined investigation using the flowing afterglow technique and molecular orbital calculations (MNDO and ab initio) substitution reactions of the kind

$$Nu^- + \begin{array}{c}|\\-Si-X\\|\end{array} \longrightarrow \begin{array}{c}|\\Nu-Si-\\|\end{array} + X^-$$

have been systematically studied.[12a] It was found that exothermic substitution reactions occurred at the collision rate whereas analogous endothermic reactions were not observed in the experiment. In the latter reaction a series of pentacoordinate silicon anions were detected.

In a flowing afterglow experiment[15] the acetyl anion, CH_3CO^-, was prepared in the gas phase by allowing F^- to react with acetyltrimethylsilane. This indicates an exothermic reaction.

To our knowledge theoretical calculations contributing to the elucidation of the reaction between F^- and formylsilane have not been published previously, although results of a series of studies of anionic pentacoordinated silicon species are available.[16] The most extensive calculations have been performed on the prototype SiH_5^-, but also products arising from the addition reactions

$$X^- + SiH_4 \rightarrow [XSiH_4]^-$$

where X = H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH and Cl have

been studied.[12a,17] The stability of the pentacoordinated anion relative to departure of HX has also been evaluated by theoretical calculations. The major problems addressed in these studies are related to the stereochemistry of the substitution and the question as to whether the anion is an intermediate or a transition state for the reaction.

For computational reasons we have based our study on unsubstituted formylsilane (SiH_3CHO) as the model compound and adopted the F^- anion as the nucleophile. Formylsilanes are all very unstable, and only recently has the first stable compound of this class, the formyltris(trimethylsilyl)silane (($Me_3Si_3)_3$-SiCHO) been isolated and characterized.[18] Formylsilanes formed in situ have been used in synthetic work.[19] The model compound chosen for the present theoretical study should be relevant as changes in the substituents on the Si atom do not lead to significant differences in the observed reaction patterns of the acylsilanes.

The primary aim of this study is to obtain accurate information on geometries and energies for the primary products formed by the molecule–ion collision and to predict thermodynamic and kinetic stabilities of species that are conceivable as products by further reactions of the primary adducts. Our study does not address the problem of solvation effects which may be dramatic as the adducts are charged species. Accordingly the results obtained should be of central interest for further experimental studies in the gas phase.

Our study includes the species in Scheme IV.

Where appropriate, reference will be made also to the transcient species claimed to appear in the reactions suggested for solutions and discussed above.

Computations

Geometry optimizations within the restricted Hartree–Fock approximation and using a 6-31++G** basis set[20] were carried out for all the species included in the study. For anionic species diffuse functions are known to be important for a proper description of electron distribution and related properties, and for the sake of consistency this basis set was applied to all species included. For comparative purposes some of the anionic species were also optimized using a 6-31G** basis.[21] The optimizations were performed without any constraints, *i.e.* all the $3N - 6$ internal coordinates were relaxed. Analytically calculated vibrational frequencies were computed for all stationary points using the 6-31++G** basis set. Thus all the stationary points on the surface were properly characterized. Some of the transition states found had a very complex vibrational mode associated with the imaginary frequency. In all these cases the reactions were followed from transition state to reactant and to product along the intrinsic reaction coordinate (IRC).[22] In the stationary points energies were calculated by Møller–Plesset perturbation calculations up to fourth order and including single, double, triple, and quadruple excitations (MP4(SDTQ))[23] using the same basis. Energy differences were corrected for zero-point vibrational energies obtained using the same basis. These energies were based on unscaled vibrational frequencies. The program system Gaussian92 was used throughout the calculations.[24]

(12) (a) Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601. (b) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7711. (c) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(13) (a) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146. (b) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229. (c) DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science* **1982**, *218*, 955.

(14) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76.

(15) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385.

(16) (a) Kutzelnigg, W.; Wallmeier, H.; Wasilewski, J. *Theor. Chim. Acta* **1979**, *51*, 261. (b) Kutzelnigg, W.; Wasilewski, J. *J. Am. Chem. Soc.* **1982**, *104*, 953. (c) Shih, S. K.; Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, 261. (d) Brandemark, U.; Siegbahn, P. E. M. *Theor. Chim. Acta* **1984**, *66*, 233. (e) Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1987**, *133*, 553. (f) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889.

(17) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056.

(18) Elsner, F. H.; Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 313.

(19) Linderman, R. J.; Suhr, Y. *J. Org. Chem.* **1988**, *53*, 1569.

(20) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294.

(21) Hariharan, P. C.; Pople, J. A. *Theor. Chim Acta* **1973**, *28*, 213.

(22) (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Fukui, K.; Kato, S.; Fujimoto, H. *J. Am. Chem. Soc.* **1975**, *97*, 1. (c) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(23) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.
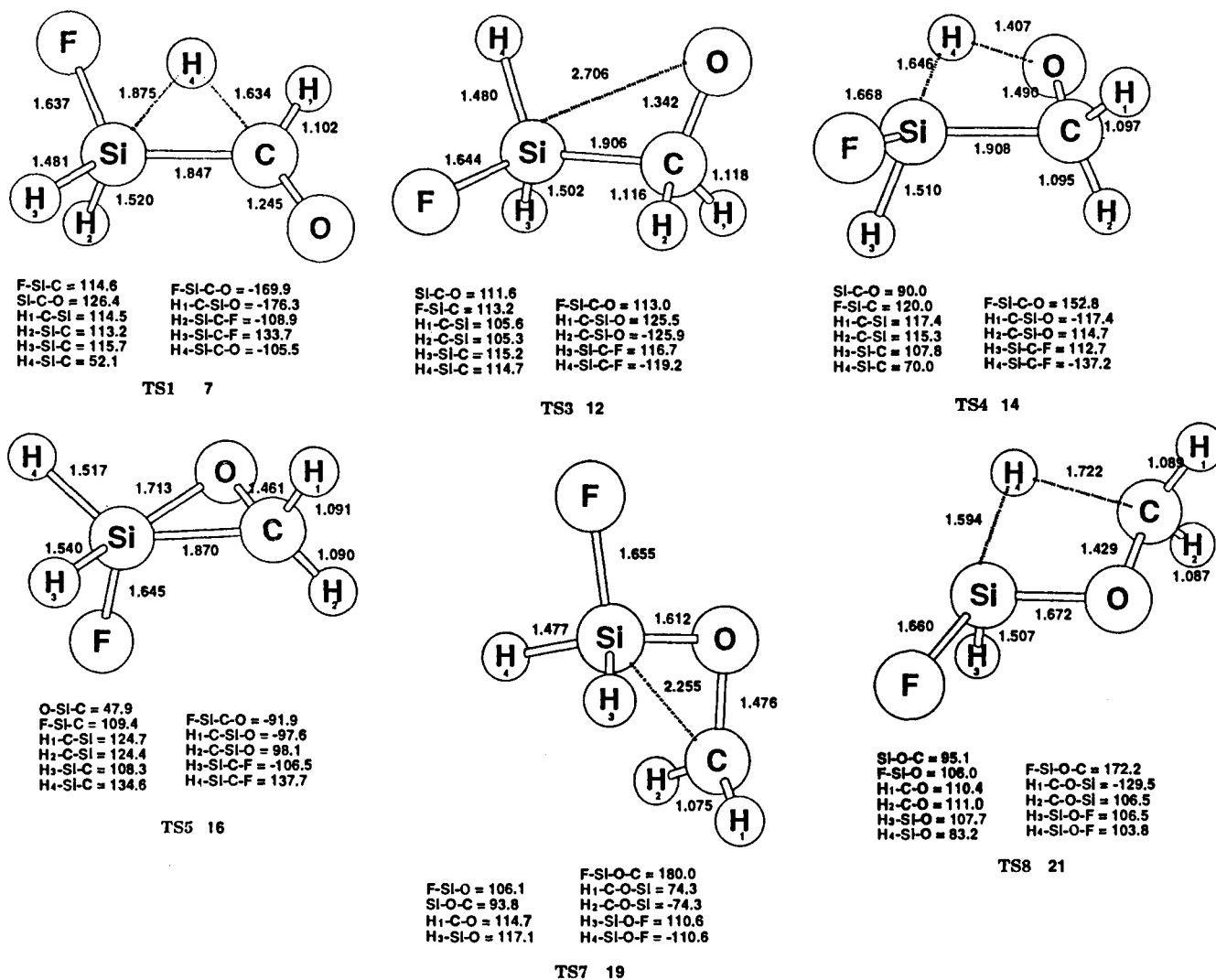
Figure 2. Transition states optimized at HF/6-31++G**. The minus signs on the anions have been omitted.

Results and Discussion

The optimized geometries are given in Figures 1–4. The calculated total energies and zero-point vibrational energies for all species included are given in Table I. In Table II energies relative to F^- + H_3SiCHO are given. A diagram displaying the relative energies for all species involved in the reaction chart presented above is given in Figure 5.

H_3Si–CHO. In this species, **2**, the carbon–silicon bond is found to be 1.928 Å, *i.e.* significantly longer than the corresponding bond in SiH_3CH_3 which optimizes to 1.887 Å using the 6-31++G** basis set. A long Si–CO(acetyl) bond of 1.926 Å is also found experimentally by X-ray analysis of acetyltriphenylsilane.[6] The carbonyl bond distance is found to be slightly longer in **2** than in acetaldehyde (1.194 Å as compared to 1.188 Å). An estimate of a possible destabilization of the carbonyl group by replacement of an α-methyl by an α-silyl may be obtained from the isodesmic equation H_3C–CHO + H_3Si–CH_3 → H_3Si–CHO + H_3C–CH_3.

Energy differences calculated at various levels of theory, with HF/6-31G* optimized geometries, show that there is an appreciable destabilization, ranging from 13.7 kcal/mol at the RHF level to 12.2 kcal/mol at the MP4(SDTQ) level. By correcting for ZPE the latter value changes to 12.5 kcal/mol. This value

is very close to a corresponding value of 12.0 kcal/mol obtained previously for the acetone system.[25]

As mentioned above, the vibrational spectra of acylsilanes show a significant lowering of the carbonyl stretching frequency as compared to the corresponding ketones. The following observed frequencies are taken from a compilation in ref 3a: Ph_3CCOPh 1692 cm⁻¹, $Ph_3SiCOPh$ 1618 cm⁻¹; Me_3CCOPh 1675 cm⁻¹, Me_3-$SiCOPh$ 1620 cm⁻¹; Me_3CCOCH_3 1710 cm⁻¹, $Me_3SiCOCH_3$ 1645 cm⁻¹. These data indicate that the observed shifts are in the range 50–80 cm⁻¹ depending on the nature of the substituent groups.

A systematic theoretical study of substituent effects on CH stretching frequencies has demonstrated the ability of theoretical methods to account for frequency shifts induced by substituents.[26]

From our analytically calculated vibrational frequencies using the 6-31G* basis we predict a carbonyl stretching frequency (unscaled) of 2030 cm⁻¹ in CH_3CHO and a corresponding value of 1960 cm⁻¹ in SiH_3CHO. Although the absolute values are inaccurate due to lack of anharmonicity and electron correlation corrections and absence of solvent interactions, the predicted lowering of 70 cm⁻¹ is in good agreement with the observed range of spectral shifts.

$(FH_3Si$–CHO)⁻. The pentacoordinate anion resulting from a nucleophilic attack on Si by F⁻ may have F in an axial or equatorial position depending on the mode of attack. Both of these isomers,

(24) *Gaussian 92*, Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B., Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. J.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc.: Pittsburgh, PA, 1992.
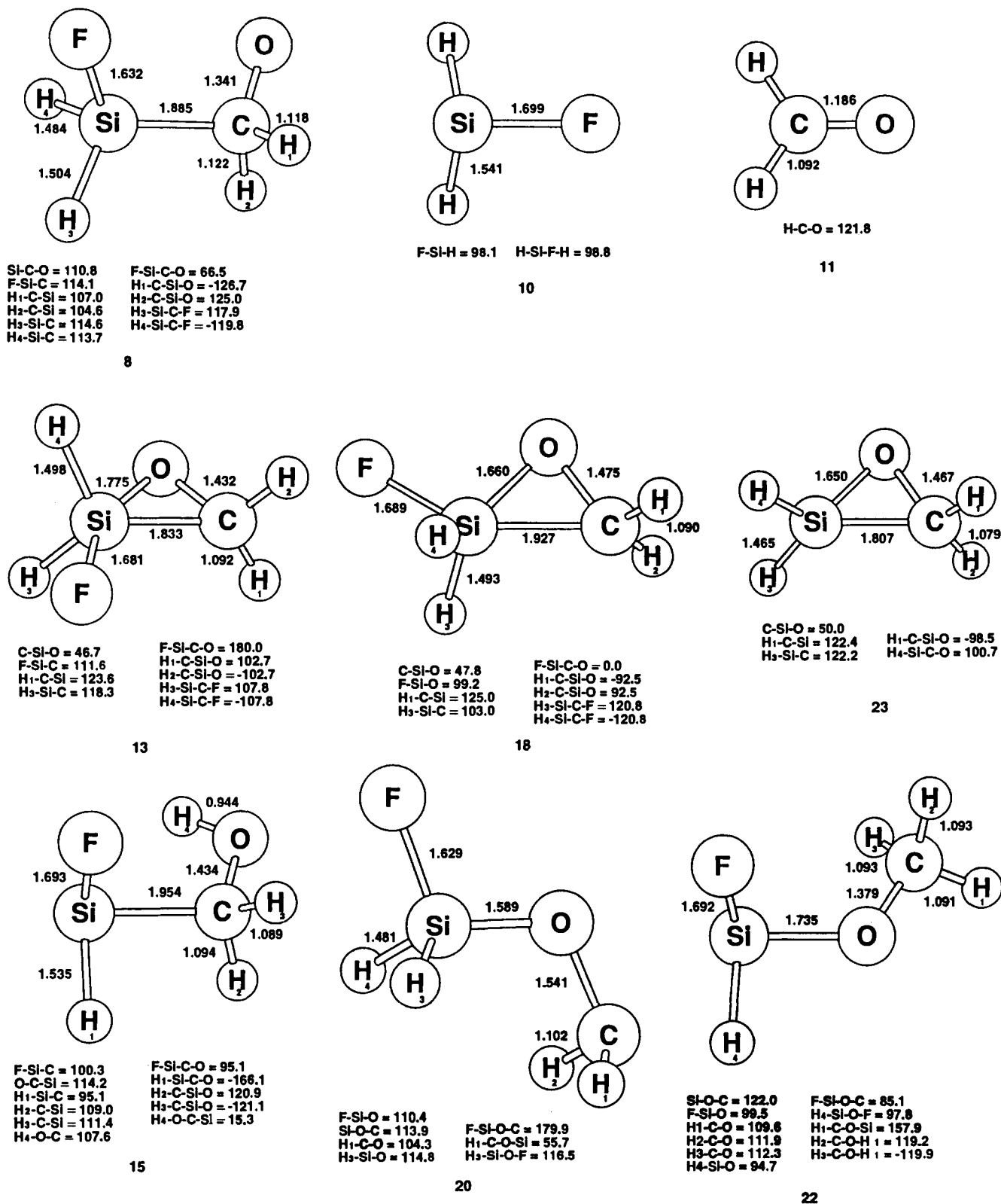
(25) Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873.
(26) Raghavachari, K. *J. Chem. Phys.* **1984**, *81*, 2717.

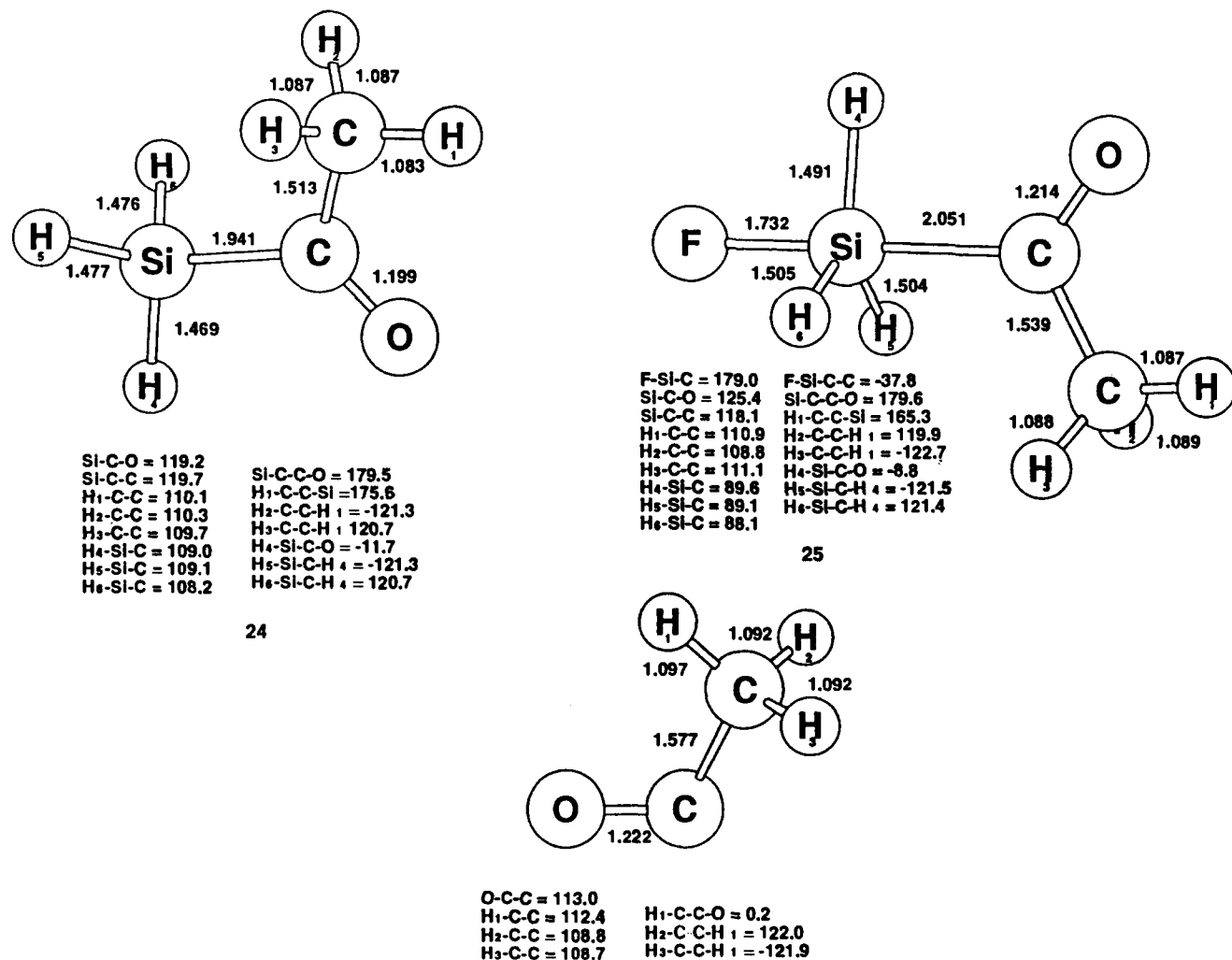**Figure 3.** Optimized geometries at HF/6-31++G**. The minus signs on the anions have been omitted.

3 and 4, respectively, have a trigonal-bipyramidal geometry as shown in Figure 1. There are two different forms of the equatorial anion, one having the F atom in a gauche position with a dihedral angle of 129.9° relative to oxygen and the other having this atom in a *cis* position. These are species 4a and 4b, respectively. All these species displayed only real vibrational frequencies. Both of the two forms of 4 have energies above the axial isomer which represents the global energy minimum of the anion. At the highest level of calculation (MP4(SDTQ) with ZPE correction) the isomer

with F in an axial position is favored by 9.8 kcal/mol relative to the most stable equatorial one, 4a.

Optimizations of 3 and 4 using the 6-31G** basis set, *i.e.* without diffuse functions, led to rather similar geometries. The largest deviation between the two sets of geometries is the elongation of the silicon–fluorine bond in 3 by around 0.04 Å after introduction of diffuse functions (1.689 to 1.726 Å). It is also worth mentioning that the ordinary basis predicts HOMOs that are strongly negative for both species, viz. –0.138 and –0.133

SI-C-O = 119.2
SI-C-C = 119.7   SI-C-C-O = 179.5
H1-C-C = 110.1   H1-C-C-SI = 175.6
H2-C-C = 110.3   H2-C-C-H1 = -121.3
H3-C-C = 109.7   H3-C-C-H1 120.7
H4-SI-C = 109.0   H4-SI-C-O = -11.7
H5-SI-C = 109.1   H5-SI-C-H4 = -121.3
H6-SI-C = 108.2   H6-SI-C-H4 = 120.7

24

F-SI-C = 179.0   F-SI-C-C = -37.8
SI-C-O = 125.4   SI-C-C-O = 179.6
SI-C-C = 118.1   H1-C-C-SI = 165.3
H1-C-C = 110.9   H2-C-C-H1 = 119.9
H2-C-C = 108.8   H3-C-C-H1 = -122.7
H3-C-C = 111.1   H4-SI-C-O = -8.8
H4-SI-C = 89.6   H5-SI-C-H4 = -121.5
H5-SI-C = 89.1   H6-SI-C-H4 = 121.4
H6-SI-C = 88.1

25

O-C-C = 113.0
H1-C-C = 112.4   H1-C-C-O = 0.2
H2-C-C = 108.8   H2-C-C-H1 = 122.0
H3-C-C = 108.7   H3-C-C-H1 = -121.9

Figure 4. Optimized geometries at HF/6-31++G**. The minus signs on the anions have been omitted.

au for 3 and 4, respectively. These values are only slightly modified by the augmented basis, the new values being –0.158 and –0.150 au, respectively.

A stationary point for **4** having F in a *trans* position to oxygen was also found. This structure displayed one imaginary frequency of 85*i* cm⁻¹, the associated normal mode of which was a twist around the Si–C bond.

The energy associated with the loss of F⁻ from the axial anion **3** is predicted to be 52.4 kcal/mol at the SCF level (6-31++G**). This value is about the same, 51.2 kcal/mol, when evaluated at the MP4 level. The latter value corrected for differences in ZPE is 50.5 kcal/mol.

In a recent systematic study[12a] of fluoride affinities, i.e. the energy relationship for loss of X⁻ from [H₃SiXY]⁻ using MNDO and ab initio calculations, it has been found that electron-withdrawing Y groups (OH, OMe, F, Cl,....) give energies rather similar to our value for X = F. Predicted values at the MP2/6-31++G(d,p)//HF/6-31G(d) level were 39.5 for Y = OH, 49.4 for Y = F, and 57.7 kcal/mol for Y = Cl.

In order to search for a possible energy barrier along the reaction path leading to the pentacoordinate Si anion, the geometry of the anion was fully optimized for a series of fixed values of the F–Si distance. The results of these calculations indicate that the F⁻ ion approaches silicon along an extension of the Si–C bond, and that during the F⁻ approach the H atoms bound to Si monotonically move from a nearly tetrahedral Si arrangement to a plane orthogonal to the F–Si–C axis, i.e. a trigonal-bypyramidal arrangement around Si. As shown in Figure 6 we do not find an energy barrier along this path. The same approach was used to analyze the energetics and geometry changes associated with a

departure of the CHO⁻ ion as the leaving group. In this process we found a smooth change to a tetrahedral geometry around Si as CHO⁻ departed. The energy change for this process, as depicted in Figure 6, shows a monotonic increase until reaching the sum of the energies for FSiH₃ and CHO⁻.

The formyl anion has been produced in the gas phase.[27] Its predominant reaction in this phase is that of a hydride donor,[28] a behavior that would interfere with its participation in the reaction discussed in the present context. Heats of formation and basicity of acyl anions have been estimated by semiempirical and theoretical calculations.[29]

The predicted reaction energy for the substitution reaction

$$F^- + H_3SiCHO \rightarrow FSiH_3 + CHO^-$$
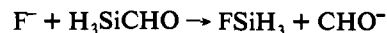
is –10.1 kcal/mol at the SCF level. This value is however shifted to only –1.0 kcal/mol at the MP4(SDTQ) level. By adding the ZEP correction the energy changes to +6.3 kcal/mol, *i.e.* an endothermic process. This suggests that the pentacoordinated anion could be a target for observation in a gas-phase experiment, using F⁻ as attacking anion provided the adduct has a possibility of dissipating its excess energy.

In order to obtain an estimate of the possible influence of substituents on the energetics of the displacement reaction, we have studied the F⁻ + H₃Si–COCH₃ system at the same

(27) Karpas, Z.; Klein, F. S. *Int. J. Mass. Spectrom. Ion Phys.* **1975**, *18*, 65.

(28) Kleingeld, J. C.; Ingemann, S.; Jalonen, J. E.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1983**, *105*, 2474.

(29) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612.

Table I. Total Energies (au) and Zero-Point Energies (kcal/mol)

		basis 6-31++G**				
		E(SCF)	E(MP2)	E(MP3)	E(MP4/SDTQ)	ZPE
F⁻	1	-99.418 586	-99.623 847	-99.613 630	-99.629 750	
H₃Si-CHO	2	-403.950 249	-404.358 241	-404.378 072	-404.403 652	28.70
E(ref) = E(1) + E(2)		-503.368 835	-503.982 088	-503.991 702	-504.033 402	28.70
(FH₃Si-CHO)⁻ax	3	-503.452 349	-504.063 752	-504.076 590	-504.114 939	29.39
(FH₃Si-CHO)⁻eq1	4a	-503.438 571	-504.048 412	-504.061 696	-504.099 803	29.06
(FH₃Si-CHO)⁻eq2	4b	-503.437 134				
FSiH₃	5	-390.159 744	-390.438 323	-390.450 116	-390.464 791	28.96
CHO⁻	6	-113.225 107	-113.544 412	-113.547 057	-113.570 239	7.08
E(5) + E(6)		-503.384 851	-503.982 735	-503.997 173	-504.035 030	36.04
(FH₂SiH-CHO)⁻ TS1	7	-503.405 649	-504.024 470	-504.034 743	-504.075 202	28.40
(FH₂Si-CH₂-O)⁻	8	-503.443 107	-504.062 047	-504.072 293	-504.110 485	31.30
(FH₂Si···CH₂O)⁻ TS2	9	-503.423 300	-504.041 349	-504.052 921	-504.093 505	30.64
H2SiF⁻	10	-389.549 470	-389.831 505	-389.842 368	-389.858 938	10.50
CH₂O	11	-113.874 716	-114.190 587	-114.196 925	-114.215 971	18.17
E(10) + E(11)		-503.424 186	-504.022 092	-504.039 293	-504.074 909	28.67
(FH₂Si-CH₂-O)⁻ TS3	12	-503.440 826	-504.059 187	-504.069 800	-504.107 524	31.37
(FH₂Si-CH₂-O)⁻cycl 1	13	-503.465 168	-504.089 330	-504.100 073	-504.135 653	32.54
(FHSi-CH₂-O···H)⁻ TS4	14	-503.379 095	-504.023 004	-504.027 872	-504.072 003	30.47
(FHSi-CH₂-OH)⁻	15	-503.454 262	-504.065 698	-504.084 280	-504.116 253	30.37
(H₂FSi-CH₂-O)⁻cycl TS5	16	-503.450 579	-504.071 840	-504.083 467	-504.118 172	31.65
(H₂FSi-CH₂-O)⁻cycl TS6	17	-503.422 019				32.50
(FH₂Si-CH₂-O)⁻cycl₂	18	-503.467 647	-504.089 528	-504.101 173	-504.135 900	31.69
(FH₂Si-O-CH₂)⁻ TS7	19	-503.428 018	-504.050 304	-504.061 588	-504.096 348	32.48
(FH₂Si-O-CH₂)⁻	20	-503.435 109	-504.049 177	-504.061 912	-504.097 169	31.16
(FHSi-O-CH₂···H)⁻ TS8	21	-503.384 683	-504.022 831	-504.032 534	-504.070 781	34.28
(FHSi-O-CH₃)⁻	22	-503.490 753	-504.102 347	-504.119 054	-504.152 411	31.65
(H₂Si-CH₂-O)cycl	23	-403.944 247	-404.366 008	-404.383 693	-404.407 697	31.69
E(1) + E(23)		-503.362 833	-503.989 855	-503.997 323	-504.037 447	31.69
H₃Si-C(CH₃)O	24	-443.000 948	-443.555 056	-443.584 585	-443.617 181	47.38
(FH₃Si-C(CH₃)O)⁻	25	-542.498 189	-543.256 285	-543.279 146	-543.324 276	48.34
CH₃CO⁻	26	-152.276 792	-152.747 223	-152.758 021	-152.790 499	27.29
E(1) + E(24)		-542.419 534	-543.178 903	-543.198 215	-543.246 931	47.38
E(5) + E(26)		-542.436 536	-543.185 546	-543.208 137	-543.255 290	56.25

Table II. Relative Energies (kcal/mol)

		E(SCF)	E(MP2)	E(MP3)	E(MP4/SDTQ)	ΔZPE
E(ref) = E(1) + E(2)		0.00	0.00	0.00	0.00	0.00
(FH₃Si-CHO)⁻ax	3	-52.41	-51.24	-53.27	-51.17	0.69
(FH₃Si-CHO)⁻eq1	4a	-43.76	-41.62	-43.92	-41.67	0.36
(FH₃Si-CHO)⁻eq2	4b	-42.86				
E(5) + E(6)		-10.05	-0.41	-3.43	-1.02	7.34
(FH₂SiH-CHO)⁻ TS1	7	-23.10	-26.60	-27.01	-26.23	-0.30
(FH₂Si-CH₂-O)⁻	8	-46.61	-50.18	-50.57	-48.37	2.60
(FH₂Si···CH₂O)⁻ TS2	9	-34.18	-37.19	-38.42	-37.72	1.94
E(10) + E(11)		-34.73	-25.10	-29.86	-26.05	-0.03
(FH₂Si-CH₂-O)⁻ TS3	12	-45.18	-48.38	-49.01	-46.51	2.67
(FH₂Si-CH₂-O)⁻cycl 1	13	-60.45	-67.30	-68.00	-64.16	3.84
(FHSi-CH₂-O···H)⁻ TS4	14	-6.44	-25.68	-22.70	-24.22	1.77
(FHSi-CH₂-OH)⁻	15	-53.61	-52.47	-58.09	-51.99	1.67
(H₂FSi-CH₂-O)⁻cycl TS5	16	-51.30	-56.32	-57.58	-53.19	2.95
(H₂FSi-CH₂-O)⁻cycl TS6	17	-33.37				3.80
(FH₂Si-CH₂-O)⁻cycl 2	18	-62.01	-67.42	-68.69	-64.32	2.99
(FH₂Si-O-CH₂)⁻ TS7	19	-37.14	-42.81	-43.85	-39.50	3.78
(FH₂Si-O-CH₂)⁻	20	-41.59	-42.10	-44.06	-40.01	2.46
(FHSi-O-CH₂···H)⁻ TS8	21	-9.94	-25.57	-25.62	-23.46	5.58
(FHSi-O-CH₃)⁻	22	-76.50	-75.46	-79.91	-74.68	2.95
E(1) + E(23)		3.77	-4.87	-3.53	-2.54	2.99
E(1) + E(24)		0.00	0.00	0.00	0.00	0.00
(FH₃Si-C(CH₃)O)⁻	25	-49.36	-48.56	-50.79	-48.53	0.96
E(5) + E(26)		-10.67	-4.17	-6.23	-5.25	8.87

calculational level. This system is sufficiently close to the experimentally known[15] reaction

$$F^- + (CH_3)_3Si-(CH_3)CO \rightarrow (CH_3)_3SiF + CH_3CO^-$$
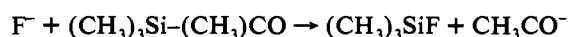
to provide a possibility for a comparison between experimentally based and theoretically suggested conclusions.

The total energies and ZPE's for acetylsilane, **24**, for the pentacoordinated adduct with F in an axial position, **25**, and for the acetyl anion, **26**, are included in Table I. The optimized geometries for these species using a 6-31++G** basis are given in Figure 4. The energies of **25** relative to E(1) + E(24) predicted at different levels, found in Table II, show that the values are very similar to those for the formyl system. At the SCF level the values are -52.4 and -49.4 kcal/mol for the formyl and acetyl systems, respectively. These values are changed to -51.2 and -48.5 kcal/mol, respectively, at the MP4 level. ZPE corrections modify these values to -50.5 and -47.6 kcal/mol, respectively.
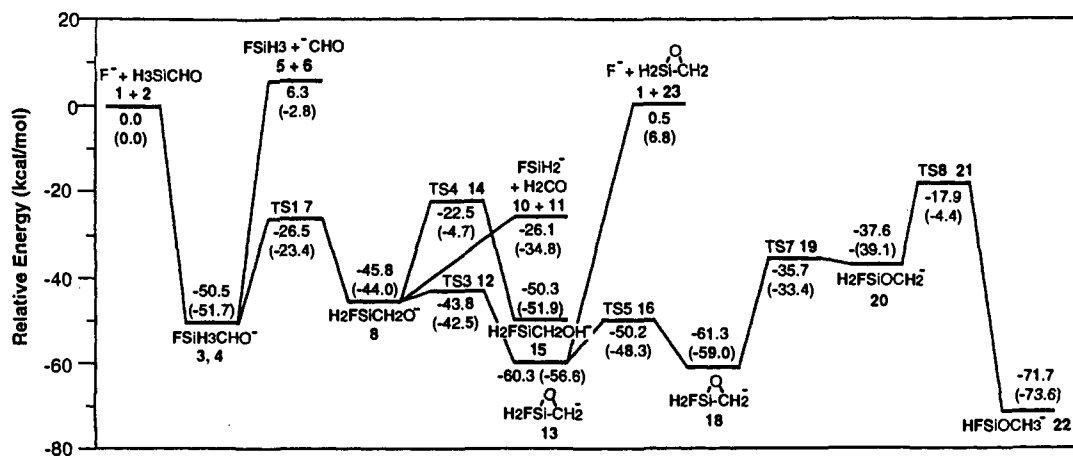
Figure 5. Theoretical estimates of relative energies in kcal/mol. Upper values refer to MP4(SDTQ) + ZPE, Lower values (in parentheses) refer to HF + ZPE.
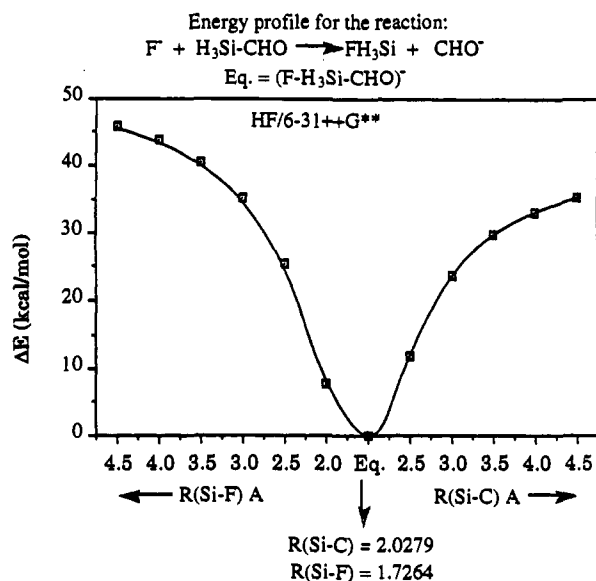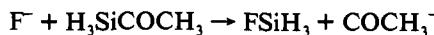

Energy profile for the reaction:
F⁻ + H₃Si-CHO ⟶ FH₃Si + CHO⁻
Eq. = (F-H₃Si-CHO)⁻

R(Si-C) = 2.0279
R(Si-F) = 1.7264

Figure 6. Energy profile for the displacement reaction F⁻ + H₃SiCHO → FH₃Si + CHO⁻.

The reaction energy for the substitution reaction

$$F^- + H_3SiCOCH_3 \rightarrow FSiH_3 + COCH_3^-$$

is predicted to be −10.7 kcal/mol at the SCF level. This value is, in the same way as for the formyl system, reduced at the MP4 level. In this case the value is −5.3 kcal/mol. By adding the ZPE correction the energy changes to +3.6 kcal/mol, *i.e.* to an endothermic process also in this case. Considering the fact that this displacement reaction is observed in the gas phase[15] and that the energetics for the formyl reaction is very similar (+6.3 kcal/mol), the latter reaction should not be excluded on the basis of its thermodynamics.

(FH₃Si–CHO)⁻ → (FH₂Si–CH₂–O)⁻. The migration of an H atom from Si to C in species **3** leads to alkoxide **8**. The energy barrier to this migration is found to be 24.9 kcal/mol at the MP4 level. This value is changed to 23.9 kcal/mol after adding ZPE corrections. The geometry of the TS, **7**, shows an appreciable shortening of the Si–C bond and a lengthening of the C–O bond as compared to those of the pentacoordinated anion. In the TS the migrating H is roughly midway between Si and C, and the arrangement around Si has to a large extent changed toward tetrahedral.

The resulting alkoxide **8** has an energy that is 2.8 kcal/mol above that of the pentacoordinated anion predicted at the MP4 level. ZPE corrections changed this value to 4.7 kcal/mol.

(FH₂Si–CH₂–O)⁻. Alkoxide **8** may undergo a series of different reactions. As shown in the chart above we have studied the dissociation process leading to the FH₂Si⁻ ion **10** and formaldehyde **11**, the rearrangement leading to the ring closure product **13**, and the proton migration leading to alcohol **15**.

Optimization at the HF/6-31++G** level along the dissociation path led to a stationary point on the surface corresponding to species **9**. This species has one imaginary frequency of 227*i* cm⁻¹, the associated mode of which is a Si–C stretching vibration. Thus it is a proper TS for the dissociation. Its energy at the SCF level is only 0.5 kcal/mol above the sum of the energies for the dissociation products **10** and **11**. By introduction of correlation energy the relative energy of the TS is lowered far more than that of the dissociation products, ending up below the sum of their relative energies. The energy of species **9** relative to alkoxide **8** is only slightly changed by going beyond the SCF level. Thus our results give us reason to conclude that the energetics of the dissociation reaction is that of an uphill process.

The reaction path leading to ring closure goes through TS3, species **12**, which has an energy only slightly above alkoxide **8**, the barrier being 1.4 kcal/mol at the SCF level and changing to 1.9 kcal/mol at the MP4 level. ZPE corrections bring about a change of only about 0.1 kcal/mol, the final value being 2.0 kcal/mol. The small value obtained indicates that the barrier may disappear at higher calculational levels. As shown in Figures 2 and 3 the geometries of **8** and **12** are rather similar, the main difference being a rotation of the H₂FSi group relative to the CH₂O moiety. In the local minimum **8** the dihedral angle F–Si–C–O is 66.5° and in the TS it is 113.0°.

(FH₂Si–CH₂–O)⁻. IRC following from **12** leads to the 3-membered ring anion **13** which has a relative energy of −60.4 kcal/mol, *i.e.* a stabilization of 13.8 kcal/mol relative to the alkoxide at the SCF level. This value changes to 15.8 kcal/mol at the MP4 level, a value which is modified to 14.5 kcal/mol after introduction of ZPE corrections. The ring closing process is asynchronous in the sense that the FH₂Si rotation is almost completed before the Si–C–O angle starts diminishing from the value in the TS. To our knowledge the cyclic anion **13** has never been detected or described before. However, cyclic silanes with 4- and 6-membered carbon rings have been made and studied.[30] In a gas-phase reaction between F⁻ and 1,1-dimethylsilacyclobutane 40% of the end products was represented by the pentacoordinated adduct. In the same paper the F⁻ affinity of the silacyclobutane was estimated to be 40 kcal/mol, a value significantly larger than the one for silacyclohexane.[30] This large difference is interpreted in terms of relief of ring strain in the 4-membered ring as it is permitted to span one axial and one

(30) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

equatorial position in the trigonal bipyramidal adduct. Our predicted F⁻ affinity of **23** of 64.2 kcal/mol at the SCF level fits nicely in to this sequence as the strain in the 3-membered ring is larger. The affinity at the MP4 level is predicted to be 61.6 kcal/mol. This value is modified to 60.8 kcal/mol after addition of ZPE corrections. This large energy difference reflects the release of ring strain as the Si atom changes from a tetrahedral arrangement in **23** to a deformed bipyramidal arrangement in **13**. The optimized geometry of **13** shows a deformed trigonal-bipyramidal arrangement around Si with virtual coplanarity of H_2–Si–C and H–Si bond lengths corresponding to the equatorial ones in **3** and **4**. The F–Si–C axis in **13** is bent due to ring closure which is energetically favored by the formation of a strong Si–O bond.

Silaoxirane anion **13** may convert to its isomer **18** by two different reaction channels, *viz.* rotation of the SiH_2F group going through TS5, species **16**, and penetration of the F-atom through the H_2Si plane the TS of which is TS6, species **17**. Calculations at the SCF level gave a strong energetic preference for TS5, **17** having an energy of around 18 kcal/mol above **16**. Higher level calculations on **17** were therefore not pursued. The barrier to interconversion along the rotation path was found to be 11.0 kcal/mol at the MP4 level. This value shifted to 10.1 kcal/mol when ZPE corrections were included.

The Si–O bond length in **18**, 1.660 Å, is appreciably shorter than that in **13** where the oxygen adopts an axial position and the length is predicted to be 1.775 Å. The reverse change takes place for the Si–C bond which goes from 1.927 Å in **13** to 1.833 Å in **18**.

The ring opening of anion **18** goes through ether type carbanion **19**. This TS represents a barrier of 24.9 kcal/mol at the SCF level. This value remains unchanged at the MP4 level and is increased to 25.6 kcal/mol after incorporating ZPE corrections.

$(H_2FSi–O–CH_2)^-$. IRC following from TS7, **19**, leads to ether type carbanion **20**. Its relative energy is predicted to be –41.6 kcal/mol at the SCF level and –40.0 kcal/mol at the MP4 level. ZPE corrections modify the latter value to –37.6 kcal/mol. This implies that the barrier to ring closure of **20** is very low, only 1.9 kcal/mol at the MP4 level invoking ZPE corrections.

$(H_2FSi–O–CH_2)^- \rightarrow (HFSi–O–CH_3)^-$. An alternative rearrangement of **20** that we have studied is the 1,3-migration of an H-atom from Si to C leading to methyl ether anion **22**. The barrier for this process going through TS8, species **21**, is predicted to be rather high. At the SCF level we find a barrier of 31.7 kcal/mol, modified to 16.6 kcal/mol at the MP4 level. This value is shifted to 19.7 kcal/mol after introduction of ZPE corrections.

The methyl ether, **22**, is the most stable of the species included in our reaction scheme having a relative energy of –74.7 kcal/mol at the MP4 level. This value is modified to –71.7 kcal/mol after invoking ZPE corrections.

$(FH_2Si–CH_2–O)^- \rightarrow (FHSi–CH_2–OH)^-$. The third type of rearrangement of alkoxide **8** that we have studied is the 1,3-

migration of an H atom from Si to O leading to alcohol **15**. The TS, species **14**, has an energy that is 40.2 kcal/mol above **8** at the SCF level. The barrier at the MP4 level is reduced to 24.2 kcal/mol, a value which is further lowered to 23.3 kcal/mol after introducing ZPE corrections. This barrier is about the same as those predicted for the other H atom migrations included in this study, *viz.* TS's **7** and **21**.

Alcohol **15** is predicted to have a relative energy of –53.6 kcal/mol at the SCF level, a value which is modified to –52.0 kcal/mol at the MP4 level. This value is further changed to –50.3 kcal/mol after invoking corrections for ZPE.

Energy Diagram in Relation to Solution Processes. One of the crucial steps involved in the acylsilane reactions in solutions is the Brook rearrangement involving a Si-moiety migration from carbon to oxygen (Schemes I and IIb). This step would correspond to a direct transformation of alkoxide **8** to carbanion ether **20**. As discussed above, both of these species have very low barriers, 2.0 and 1.9 kcal/mol, respectively, to ring closures giving the very stable species **13** and **18**, respectively. Thus it seems unlikely that a direct process of this kind involving a TS having a 3-membered ring structure would occur in the gas phase. The stabilization of such a structure must involve intermolecular interactions which are likely to be large for these anionic species in solution.

Conclusions

The main findings of the present investigation are the following:

1. The addition of F⁻ to formylsilane occurs without an energy barrier. The resulting pentacoordinated anion prefers to have the F atom in an axial position. The departure of the formyl anion as a leaving group from the adduct is energetically an uphill process. The displacement reaction is predicted to be endothermic, but with a very small reaction energy (6.3 kcal/mol). Addition of F⁻ to and displacement of acetyl anion from acetylsilane has an energy profile that is very similar to the formyl system. This reaction is also endothermic with a very small reaction energy (3.6 kcal/mol).

2. We have not been able to locate a transition state relevant for the direct migration of a silicon group from carbon to oxygen. Such a migration has been invoked in the proposed mechanism for acylsilane reactions in solutions (Brook rearrangement).

3. We predict the possible existence of several anions that are thermodynamically stable relative to F⁻ and formylsilane. Of these we mention the 3-membered rings **13** and **18** which can be reached from the initially formed adduct by passing a barrier of around 25 kcal/mol.