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Experimental and Theoretical Studies of $SiF_n(CO)_2^+$ Cations with $n = 2$ and 3: A Search for Pentacoordinate Cationic Silicon

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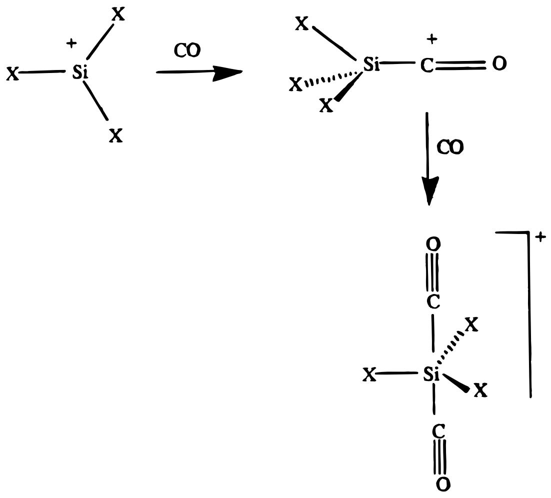
The addition of carbon monoxide to the fluorosilicon cations SiF^+, $SiF_2^{\bullet+}$, and SiF_3^+ has been investigated in helium buffer gas at (294 ± 3) K and (0.35 ± 0.01) Torr using a selected-ion flow tube (SIFT) apparatus. The monofluorosilicon cation was found to be unreactive toward CO, whereas both the difluoro- and trifluorosilicon cations consecutively added two CO molecules. Molecular orbital calculations, using density functional theory (DFT) performed at the B-LYP/6-31G(d,p) level, showed that the lowest-energy isomer on the $SiF_3(CO)_2^+$ potential energy surface has a trigonal bipyramidal structure in which a pentacoordinate Si atom is surrounded by two axial CO ligands (bonded through C) and three equatorial F substituents. The ion at the global minimum on the $SiF_2(CO)_2^{\bullet+}$ potential energy surface has a structure between that of a distorted tetrahedron and a trigonal bipyramid in which both CO molecules are axial and the two fluorine atoms and the unpaired electron are equatorial. Other low-lying isomers have trigonal bipyramidal structures in which one or both CO ligands are bonded to silicon through oxygenn or have tetrahedral structures in which an F_3SiCO^+ or $F_2SiOC^{\bullet+}$ ion is solvated by CO. A multicollision-induced dissociation (CID) study of the product $SiF_3(CO)_2^+$ indicated the presence of at least three structural isomers, whereas the CID of $SiF_2(CO)_2^{\bullet+}$ was less conclusive.

Introduction

Silicon, like several second-row elements, is hypercoordinate in a variety of compounds.[1,2] Such compounds have been of interest since the early 19th century, stimulated by the discoveries by Gay-Lussac and by Davy of the hexacoordinate anion SiF_6^{2-} and of an SiF_4-NH_3 addition complex.[3,4] More recently, considerable experimental effort has been expended on the synthesis of hypercoordinate silicon-containing species, primarily in solution[2a−e,g−n,p−u] and also in solid crystal lattices.[2b,f−h,m,o] These have been complemented by several theoretical studies on hypercoordinate silicon-containing neutrals[2b,e,5a] and anions.[2b,e,v,x−z,5]

Experimental studies of pentacoordinate silicon-containing cations are relatively rare compared with those of neutral molecules and anions, and of the studies reported, none are for the gas phase.[2b,d,i,p,s−u,w] Furthermore, a search of the ab initio molecular orbital literature on pentacoordinate silicon-containing cations has located few theoretical studies.[2n,6] A high-level theoretical study of the parent silonium ion, SiH_5^+, showed the structure at the global minimum to have three short Si−H bonds and two long Si−H bonds, but with the loosely attached H atoms close together, i.e., essentially a trigonal SiH_3^+ ion weakly solvated by H_2.[6] The pentacoordinate structure with D_{3h} symmetry, the classical trigonal bipyramidal structure, was found to be approximately 80 kcal mol^{-1} higher in energy and to have three imaginary frequencies. This apparent reluctance of Si to form cations in which the coordination number exceeds four, despite the large number of neutral molecules and anions in which the coordination number of Si is larger, intrigued us. In principle, there seemed to be no reason why pentacoordinate Si^+ should not be formed by the addition of two ligands such as carbon monoxide to a silyl cation as in eq 1.



....(1)

A judicious choice for X would be an electronegative atom or group that can withdraw electron density from the already electron-deficient Si center, thereby enhancing the electrophilicity of the Lewis acid. Plausible choices for X include halogen atoms, as well as the "pseudohalide" CN group. Possible axial ligands such as NH_3 and H_2O were found to react with SiF_3^+ and led to replacement of F by NH_2 or OH and elimination of HF.[7] Carbon monoxide is a weaker ligand, but any adduct formed, either an acylium ion, F_3SiCO^+ or a solvated ion, $F_3Si^+\cdots CO$, is potentially more stable, since it is unlikely to undergo any simple elimination reaction other than reversal by loss of CO. A further addition of CO could then potentially produce the pentacoordinate $SiF_3(CO)_2^+$ cation, as shown in eq 1.

Previous experimental studies of similar non-silicon-containing Lewis acid−base reactions in which the base is carbon monoxide are documented in the chemical literature but are not

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plentiful.[8a−c] Theoretical studies of possible products of such reactions, both with silicon[8d,e] and without,[8e,f] also have been performed. Previously, in a preliminary report, we have investigated, both experimentally and theoretically, the reaction depicted in the first step of eq 1 (X = F).[9] Now, we present the results of our combined experimental and theoretical investigations of ions SiF_3^+, $SiF_2^{\bullet+}$, and SiF^+ with CO.

Experimental Methods

The gas-phase ion−molecule reactions of $SiF^+ + CO$, of $SiF_2^{\bullet+} + CO$, and of $SiF_3^+ + CO$ were performed in a selected ion flow tube (SIFT) apparatus in the ion chemistry laboratory at York University.[10,11] SiF^+, $SiF_2^{\bullet+}$, and SiF_3^+ ions were produced by electron impact of a 10% mixture of SiF_4 (99.6% minimum purity, Matheson Gas Products) in He at 50 eV. The desired ions were mass-selected through a quadrupole mass filter and were introduced, via a Venturi inlet, into a flow of helium buffer gas at a pressure of (0.35 ± 0.01) Torr. Then the ions were thermalized by collisions (ca. 4×10^5 collisions) with the helium atoms before entering the reaction region further downstream. After a few milliseconds of reaction, reactant and product ions were sampled and analyzed with a second quadrupole mass filter. Rate coefficients and product distributions were measured in the usual manner.[10,11] The reactant carbon monoxide was of high purity (99.5% minimum purity, Matheson Gas Products). Bond connectivities in the product ions were investigated with multicollision-induced dissociation (CID) experiments by raising the sampling nose-cone voltage from 0 to −80 V and concomitantly varying focusing-lens voltages to prevent the introduction of mass discrimination in the detection system.[12]

Computational Methods

Molecular orbital calculations have been performed with the GAUSSIAN series of programs.[13] Geometric optimizations of all critical points associated with closed-shell species have been carried out with Becke's density functional,[14] which includes the Slater (local spin density) exchange functional[14a,b,15] with nonlocal gradient-corrected terms included[16] and the Lee−Yang−Parr method, which includes local and nonlocal gradient-corrected correlation functionals (henceforth denoted B-LYP).[17] Geometric optimizations and subsequent harmonic frequency calculations at this level of theory have been performed using the standard Gaussian split-valence 6-31G(d,p) basis set.[18] Zero-point vibrational energies (ZPE) at this level, obtained from the harmonic frequency calculations, are reported unscaled. Transition structures were located by a preliminary coarse-grid point-by-point profile analysis followed by refinement with the eigenvector-following (EF) algorithm.[19] Intrinsic reaction coordinate (IRC)[20] analyses were performed subsequently to verify the identities of the two species at local minima, which are interconverted through each of the transition structures.

Results and Discussion

Experimental. The experimental results of the rate coefficient measurements and the observed product ions are summarized in Table 1.

$SiF^+ + CO$. The monofluorosilicon cation, SiF^+, was found to be unreactive with carbon monoxide under the SIFT experimental conditions, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

$SiF_2^{\bullet+} + CO$. A plot of observed ion-signal intensities versus CO flow rate for this reaction is shown in Figure 1. At low CO flow rates, this graph illustrates the decay of a primary reactant ion of $m/z = 66$ ($SiF_2^{\bullet+}$) accompanied by the rise of a primary product ion of $m/z = 94$ ($SiF_2(CO)^{\bullet+}$). Higher neutral flow rates result in the rise of a secondary product ion signal of $m/z = 122$ ($SiF_2(CO)_2^{\bullet+}$). No further reactions were observed. The effective bimolecular reaction rate constant, k, for the primary addition reaction is $(3.6 \pm 1.0) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, that for the secondary addition reaction is $(2.0 \pm 0.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

Results of a multicollision CID study of the product ions $SiF_2(CO)^{\bullet+}$ and $SiF_2(CO)_2^{\bullet+}$ are shown in Figures 2 and 3. The CID spectrum of $SiF_2(CO)^{\bullet+}$ in Figure 2 suggests the presence of two isomers for this ion with distinctly different dissociation thresholds, and a peak analysis of the differentiated profile indicates a relative population of 65:35. In this analysis the differentiated profile was fitted with two Maxwellians and the relative population was extracted from the relative areas of the two Maxwellians. Also, the cross sections for dissociation were assumed to be equal for the two isomeric ions. The CID spectrum shown in Figure 3 clearly demonstrates sequential loss of two CO molecules from $SiF_2(CO)_2^{\bullet+}$. The interpretation of

TABLE 1: Rate Coefficients and Efficiencies for Reactions of SiF_n^+ and $SiF_n(CO)^+$ Ions with CO

reactant ion	product ion	k_{exp}[a]	k_c[b]	k_{exp}/k_c[c]
	Primary Processes			
SiF^+	none (<0.1%)			
$SiF_2^{\bullet+}$	$SiF_2(CO)^+$	0.0036	7.6	0.00047
SiF_3^+	$SiF_3(CO)^+$	0.41	7.4	0.055
	Secondary Processes			
$SiF_2(CO)^{\bullet+}$	$SiF_2(CO)_2^{\bullet+}$	0.0020	7.3	0.00027
$SiF_3(CO)^+$	$SiF_3(CO)_2^+$	0.0041	7.1	0.00058

[a] The k_{exp} values are the measured effective bimolecular reaction rate coefficients at a temperature of (294 ± 3) K and at a helium buffer gas pressure of (0.35 ± 0.01) Torr and are reported in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. The absolute accuracies of these rate coefficients are estimated to be less than ±30%; relative accuracies are smaller than ±10%. [b] The collision rate coefficients, k_c, are derived from ADO theory (Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347). [c] k_{exp}/k_c ratios are measures of reaction efficiencies.

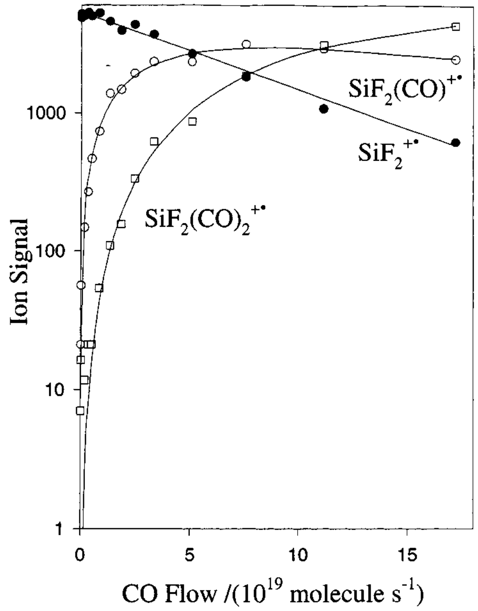

Figure 1. Data recorded for the reactions of $SiF_2^{\bullet+}$ and the adduct $SiF_2(CO)^{\bullet+}$ with carbon monoxide in helium buffer gas at (295 ± 2) K and (0.35 ± 0.01) Torr. The $SiF_2^{\bullet+}$ ions were produced in a low-pressure electron-impact ion source at 50 eV from a mixture of SiF_4 (10%) in He. The solid lines represent a fit to the experimental data with the solutions of the differential equations appropriate for the observed reaction sequence.

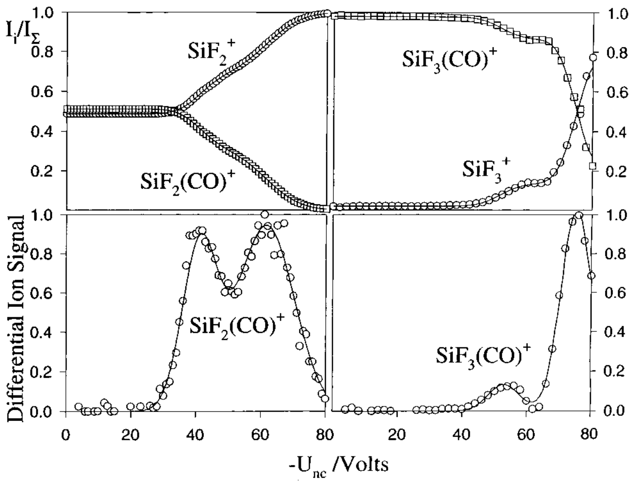

Figure 2. Results of multicollision CID experiments with $SiF_2(CO)^{\bullet+}$ produced from the reaction of $SiF_2^{\bullet+}$ with CO (left-hand side) and $SiF_3(CO)^+$ produced from the reaction of SiF_3^+ with CO (right-hand side). Helium was used as the buffer/collision gas at (295 ± 2) K and (0.35 ± 0.01) Torr. The flow of CO is 4 × 10^{19} and 2.4 × 10^{18} molecules s^{-1}, respectively. The measured fractional ion signal (top) and the normalized derivative of this signal multiplied by −1 (bottom) are plotted against the nose-cone voltage.

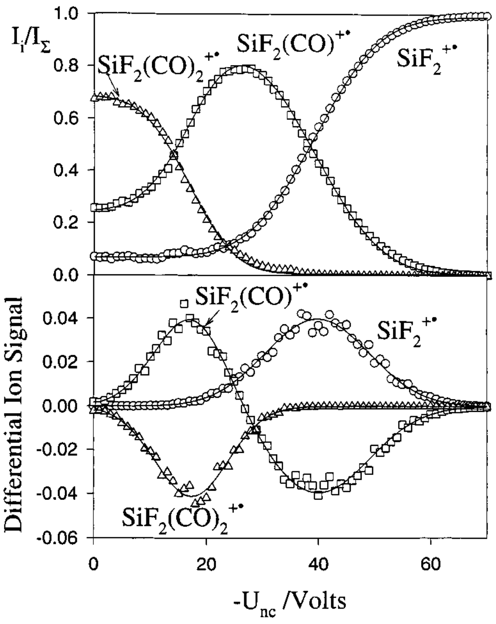

Figure 3. Results of multicollision CID experiments with $SiF_2(CO)_2^{\bullet+}$ produced from the reaction of $SiF_2(CO)^{\bullet+}$ with CO. Helium was used as the buffer/collision gas at (295 ± 2) K and (0.35 ± 0.01) Torr. The flow of CO was 14.5 × 10^{19} molecules s^{-1}. The measured fractional ion signals (top) and the derivatives of these signals (bottom) are plotted against the nose-cone voltage.

the $SiF_2(CO)_2^{\bullet+}$ profiles with regard to the presence of isomers is less straightforward. The differentiated profile does not indicate the presence of more than one isomer, although within the scatter of the data, the presence of more than one isomer with nearly overlapping dissociation thresholds cannot be completely ruled out .

SiF_3^+ + CO. A plot of observed product ion intensities versus CO flow rate is shown in Figure 4. This plot, at low neutral flow rates, shows the decay of a primary reactant ion of *m*/*z* = 85 accompanied by the rise of the signal of a primary product ion of *m*/*z* = 113. At higher CO flow rates, a rise in a secondary product ion signal, of *m*/*z* = 141, was noted. No further reactions were observed. The effective bimolecular rate coefficient, *k*, for the primary reaction is (4.1 ± 1.2) × 10^{-11} cm^3 molecule^{-1} s^{-1}; that for the secondary reaction is (4.1 ± 1.2) × 10^{-13} cm^3·molecule^{-1} s^{-1}.

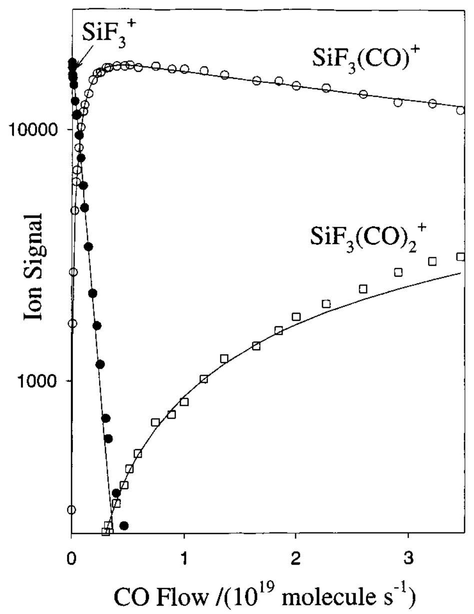

Figure 4. Data recorded for the reactions of SiF_3^+ and the adduct $SiF_3(CO)^+$ with carbon monoxide in helium buffer gas at (295 ± 2) K and (0.35 ± 0.01) Torr. The SiF_3^+ ions were produced in a low-pressure electron-impact ion source at 50 eV from a mixture of SiF_4 (10%) in He. The solid lines represent a fit to the experimental data with the solutions of the differential equations appropriate for the observed reaction sequence.

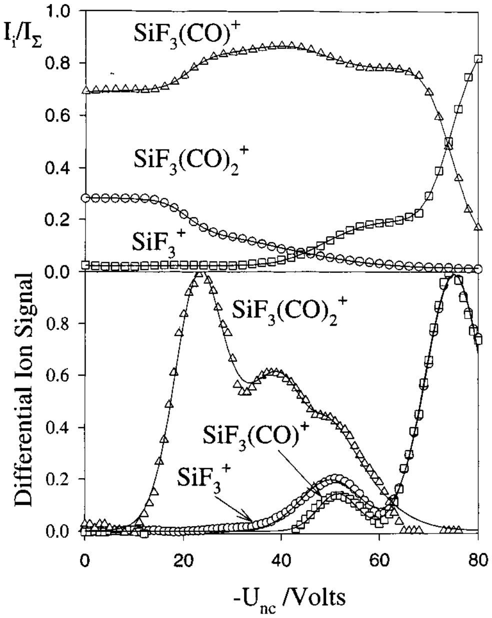

Figure 5. Results of multicollision CID experiments with $SiF_3(CO)_2^+$ produced from the reaction of $SiF_3(CO)^+$ with CO. Helium was used as the buffer/collision gas at (295 ± 2) K and (0.35 ± 0.01) Torr. The flow of CO was 6 × 10^{19} molecules s^{-1}. The measured fractional ion signals (top) and the normalized derivatives of these signals multiplied by −1 in the case of $SiF_3(CO)_2^+$ (bottom) are plotted against the nose-cone voltage.

Results of a multicollision CID study of the product ions $SiF_3(CO)^+$ and $SiF_3(CO)_2^+$ are shown in Figures 2 and 5. The CID spectrum of $SiF_3(CO)^+$ in Figure 2 suggests the presence of two isomers for this ion with distinctly different dissociation thresholds. A previous analysis of the differentiated profiles indicated a relative population of 85:15 in this case.[9] Equal CID cross sections are assumed for the two isomeric ions. The

TABLE 2: Energies[a,b] Used in Constructing the F$_3$Si(CO)$_n^+$ Potential Energy Hypersurfaces

molecule	E(B-LYP/6-31G(d,p))	ZPE[b]	rel energy wrt **1** and **3**, respectively
	Monoadduct		
F$_3$SiCO$^+$, **1**	−702.140 55	10.7	0.0
F$_3$SiOC$^+$, **2**	−702.110 96	10.0	17.8
F$_3$Si$^+$ + CO	−702.067 18[c]	8.84	44.1
	Diadduct		
(OC−SiF$_3$−CO)$^+$, **3**	−815.468 85	15.3	0.0
F$_3$SiCO$^+$···CO, **4**	−815.449 00	14.6	11.8
(OC−SiF$_3$−OC)$^+$	−815.447 94	14.5	12.3
F$_3$SiCO$^+$···OC	−815.442 99	14.3	15.2
F$_3$SiCO$^+$ + CO	−815.434 94[c]	13.7[c]	19.7[c]
(CO−SiF$_3$−OC)$^+$	−815.423 16	14.0	27.4
F$_3$SiOC$^+$···CO	−815.414 92	13.7	32.2
F$_3$SiOC$^+$···OC	−815.411 38	13.5	34.3
F$_3$SiOC$^+$ + CO	−815.404 95	13.0	37.8

[a] Total energies are in hartrees, and zero-point and relative energies are in kcal mol^{-1}. [b] From harmonic frequency calculations. Unscaled. [c] Calculated using the following total energies and ZPE: E(CO) = −113.293 99 hartrees, ZPE = 3.0 kcal mol^{-1}; E(SiF$_3^+$) = −588.773 19 hartrees, ZPE = 5.8 kcal mol^{-1}.

TABLE 3: Energies Used in Constructing the SiF$_2$(CO)$_n^{\bullet+}$ Potential Energy Hypersurfaces

molecule	E(UB-LYP/6-31G(d,p))	ZPE[a]	rel energy wrt **5** and **7**, respectively
	Monoadduct		
F$_2$SiCO$^{\bullet+}$, **5**	−602.198 08	8.0	0.0
F$_2$SiOC$^{\bullet+}$, **6**	−602.171 57	7.1	15.7
SiF$_2^{\bullet+}$ + CO	−602.142 83[b]	6.1[b]	32.8[b]
	Diadduct		
F$_2$Si(CO)$_2^{\bullet+}$,**7**	−715.532 49	12.8	0.0
F$_2$SiCO$^{\bullet+}$···CO, **8**	−715.505 93	11.8	15.7
F$_2$SiCO$^{\bullet+}$···OC	−715.500 89	11.3	18.3
F$_2$SiCO$^{\bullet+}$ + CO	−715.492 07[b]	11.0[b]	23.6[b]

[a] From harmonic frequency calculations. Unscaled. [b] E(SiF$_2^{\bullet+}$) = −488.848 84 hartrees; ZPE = 3.1 kcal mol^{-1}.

CID spectrum shown in Figure 5 demonstrates the sequential loss of two CO molecules from SiF$_3$(CO)$_2^+$. Also, the presence of a number of isomers is indicated for both the initial SiF$_3$(CO)$_2^+$ ion formed in the addition reaction of SiF$_3$(CO)$^+$ with CO and the intermediate SiF$_3$(CO)$^+$ ion formed by the collision-induced dissociation of SiF$_3$(CO)$_2^+$. Inspection of the SiF$_3$(CO)$_2^+$ profile (Figure 5, top), and particularly its differentiated form (Figure 5, bottom), reveals the presence of at least three, perhaps four, isomers with noticeably different dissociation thresholds. The dissociation of these SiF$_3$(CO)$_2^+$ isomers by loss of CO appears to lead to two isomers of SiF$_3$(CO)$^+$ with dissociation thresholds essentially identical with those for the two isomers of SiF$_3$(CO)$^+$ produced in the direct reaction of SiF$_3^+$ with CO (see Figure 2).[9]

Theoretical. *Geometries of SiF$_n$(CO)$_m^+$ (n = 2, 3; m = 0, 1, 2).* Ab initio molecular orbital calculations provide insight into the relative energies and thermodynamic stabilities of trigonal bipyramidal and tetrahedral structures for the CO adducts of SiF$_3^+$ and SiF$_2^{\bullet+}$. The computed relative energies are summarized in Tables 2 and 3. Geometric parameters for some of the SiF$_n$(CO)$_m^+$ ions are presented in Figure 6.

(SiF$_3^+$ + nCO) Potential Energy Hypersurfaces. SiF$_3^+$ is planar and addition of one CO molecule to form the acylium ion (structure **1**) results in a slight elongation of the Si−F distance (from 1.555 to 1.571 Å) and a slight decrease in the CO distance (1.150 to 1.133 Å), consistent with the transfer of some of the positive charge onto the CO (+0.374 from a Mulliken population analysis). However, the FSiC angle in F$_3$SiCO$^+$ of 100.4° is much smaller than the ideal tetrahedral angle and the Si−C distance (2.021 Å) is considerably longer than that in silaethane (1.867 Å).[21] These structural parameters indicate a relatively weak Si−C bond, and this is supported by the calculated dissociation energy of 44.1 kcal mol^{-1} at 0 K (Table 2).

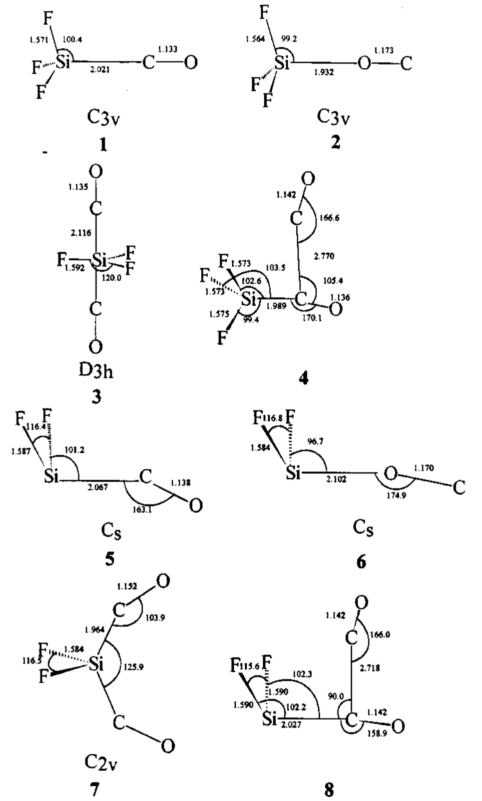

Figure 6. Key structural parameters for cations **1**−**8** from optimization at B-LYP/6-31G(d,p). Bond lengths are in angströms and angles in degrees. Ion SiF$_3^+$ has D_{3h} symmetry with an Si−F distance of 1.555 Å. Ion SiF$_2^{\bullet+}$ (C_{2v} symmetry) has an Si−F distance of 1.577 Å and an angle of 120.3°. CO has a bond distance of 1.150 Å.

Ion F$_3$SiCO$^+$, **1**, has an energy lower than that of isomer F$_3$SiOC$^+$, **2**, by 17.8 kcal mol^{-1}. This is consistent with the multicollision CID results for the mixture of F$_3$SiCO$^+$ isomers generated from addition of CO to SiF$_3^+$, which indicate a relative abundance ratio of approximately 85:0.15 for these two isomers under SIFT conditions.[9]

Addition of a second CO can, in principle, lead to formation of either an ion in which the Si is pentacoordinate, ion **3**, or an ion−molecule complex, **4**. Both **3** and **4** could have attachment to the second CO through either oxygen or carbon, but our computations show that for the (SiF$_3^+$ + nCO) potential energy surfaces the preferred attachment is through carbon, as is generally the case when CO is a ligand in transition-metal complexes.[22−29] Preliminary results indicate a similar situation for the (SiF$_2^{\bullet+}$ + nCO) potential energy surfaces. Energies computed for all of the various possible structural isomers of SiF$_3$(CO)$_2^+$, including covalently bonded and solvated isomers, are given in Table 2 and Figure 7. These results can account for the various isomers of SiF$_3$(CO)$_2^+$ identified in the CID spectrum of this ion (Figure 5). We can expect possibly as many as three covalently bonded and four solvated isomers to be formed in the reaction of SiF$_3$(CO)$^+$ with CO, since SiF$_3$(CO)$^+$ itself is a mixture of the two isomers F$_3$SiCO$^+$, **1**, and F$_3$SiOC$^+$, **2**. However, the actual assignment of structures to the three (or possibly four) isomers evident in the CID spectrum is problematic. The largest population in the dif-

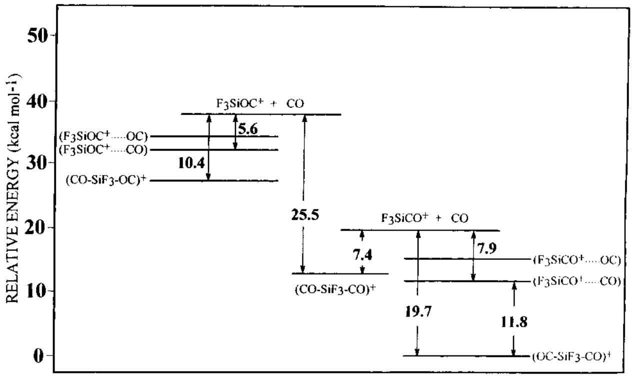

Figure 7. Relative energies (in kcal mol^{-1}) of isomers on the $F_3SiC_2O_2^+$ potential energy surface.

ferential spectrum in Figure 5 has the lowest dissociation threshold and may correspond to one or more solvated structures that have calculated dissociation energies of $\leq$7.9 kcal mol^{-1}, or even to the covalently bonded $(CO-SiF_3-CO)^+$ isomer, which has a calculated dissociation energy of 7.4 kcal mol^{-1}. The less abundant populations with higher dissociation thresholds could correspond to the covalently bonded isomers $(CO-SiF_3-OC)^+$ and $(OC-SiF_3-CO)^+$, which have computed dissociation energies of 10.4 and 19.7 kcal mol^{-1}.

The pentacoordinate ion **3** lies 11.8 kcal mol^{-1} below the solvated four-coordinate ion **4**. The latter ion has a long C$-$C distance (2.770 Å), and the F_3SiCO^+ fragment has a structure similar to that of the unsolvated ion, with the major difference being a shortening of the Si$-$C bond (from 2.021 to 1.989 Å) on solvation. Reducing the C$-$C distance in **4** to that characteristic of a single bond would lead to the 3-silatrifluoroacetoacetyl ion, $F_3SiCOCO^+$, but all attempts at optimizing this structure resulted in rearrangement to the solvated ion **4**. All the bonds in the pentacoordinate ion **3** are longer than those in F_3SiCO^+, and the axial Si$-$C distances (2.116 Å) are ~0.1 Å longer than the already long Si$-$C bond of F_3SiCO^+. These structural parameters are consistent with the relatively low energy (19.7 kcal mol^{-1} at 0 K) required to remove one CO molecule from **3**.

Our results for $SiF_3^+ + n$CO may be compared with those recently reported by Hiraoka et al. for the analogous reactions involving CF_3^+.[30] Bond energies for single and multiple adducts of CF_3^+ with CO were computed by these authors from MP4(SDQ)/6-31-G(d)//RHF/6-31G(d) electronic energies and RHF/6-31G(d) zero-point vibrational energies. Values of 15.60, 6.59, and 5.89 kcal mol^{-1} were reported for the first three adducts compared to values of 44.1 and 19.7 kcal mol^{-1} obtained here for the first two adducts of SiF_3^+. The monoadduct of CF_3^+ was shown to bond covalently through the C of CO as is the case with SiF_3^+, although in each case the C$-$C and C$-$Si distances are more than 0.1 Å longer than normal single bonds. The results for the diadducts are quite different for the two systems. Only two structures were computed by Hiraoka et al.[30] on the $CF_3(CO)_2^+$ surface, both involving attachment through the C of CO (bonding through the O of CO was not explored). These were a pentacoordinate ion, in which both the CO molecules occupy the axial position of a trigonal bipyramid, and a solvated acylium ion, and they correspond to the two structures, ions **3** and **4**, with the lowest energies on the $SiF_3(CO)_2^+$ surface. However, the solvated acylium ion, $F_3CCO^+\cdots CO$, is calculated to be 5.1 kcal mol^{-1} lower in energy than the pentacoordinate ion, $(OC-CF_3-CO)^+$, and in the latter C$-$C distances of 2.78 Å indicate very weak interactions. By contrast, on the $SiF_3(CO)_2^+$ surface, we find here that the pentacoordinate structure, **3**, is preferred over the solvated ion **4** by 11.8 kcal mol^{-1} and the Si$-$C distances in **3** (2.116 Å) are close to that found in the acylium ion F_3SiCO^+.

Up to seven additions of CO to CF_3^+ were observed by Hiraoka et al.[30] with a pulsed electron-beam high-pressure mass spectrometer operated at CO pressures of ca. 3 Torr over a wide range in temperature from ca. 500 K to temperatures as low as ca. 65 K. However, it should be noted that only the first adduct was observed at, and above, room temperature. The observation of higher adducts required lower temperatures. We were intrigued by these results in comparison with our observation of the addition of only two molecules of CO to SiF_3^+ under SIFT conditions, and so we explored the reaction of CF_3^+ with CO in separate experiments. These experiments indicated that CF_3^+ is unreactive with CO at room temperature in helium at 0.35 Torr, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This failure to observe formation of the first adduct of CF_3^+ with CO under SIFT conditions can be understood in terms of the lower pressure of the SIFT experiments and the use of atomic helium, rather than molecular CO, as the stabilizing third body in the attempted addition reaction. The observation of the formation of two CO adducts with SiF_3^+ under SIFT conditions compared to none with CF_3^+ can be understood in terms of the larger exothermicities, 44.1 and 19.7 kcal mol^{-1}, respectively, for these two additions and the larger number of degrees of freedom in the second addition, since the lifetime of the intermediate adduct increases with increasing exothermicity and increasing number of degrees of freedom.[31]

($SiF_2^{\bullet+} + n$CO) Potential Energy Hypersurfaces. Addition of CO to $SiF_2^{\bullet+}$ ($^2A_1$) yields ion **5** as the most stable structural isomer. The two most notable structural features of this adduct are a long Si$-$C bond (2.067 Å) and a small angle FSiC (101.2°), parameters that are similar to those calculated for ion **3**. The unpaired spin density remains largely on the Si (0.713*e*), and some of the charge is transferred to the CO (+0.317)**.** The oxygen-bound ion, $SiF_2OC^{\bullet+}$, **6**, is 15.7 kcal mol^{-1} higher in energy than **5**, and dissociation of **5** into CO and $SiF_2^{\bullet+}$ is endothermic by 32.8 kcal mol^{-1} (at 0 K; see Table 3). According to the CID results in Figure 2, both of these isomers may be formed in the addition of CO to $SiF_2^{\bullet+}$ under SIFT conditions. The more abundant ion (65%) with the higher dissociation threshold should be the more stable isomer (structure **5**), while the less abundant ion (35%) with the lower dissociation threshold should have structure **6**. It is interesting to note that the populations estimated for these two isomers are more equal to each other than the populations estimated for the analogous two isomers of $SiF_3(CO)^+$, which are in a ratio of 85:15. This is consistent with a difference in energy between the two isomers of $SiF_2(CO)^{\bullet+}$ (15.7 kcal mol^{-1}) that is smaller than that for the two isomers of $SiF_3(CO)^+$ (17.8 kcal mol^{-1}).[9]

In principle, attachment of a second CO molecule to **5** and to **6** could again be either through C or O, leading to the production of three possible trigonal bipyramidal isomers and four possible solvated ions. Energies have been computed only for adducts derived from structure **5**, one covalently bonded through carbon (structure **7**) and the others through solvated ions (see Table 3). A comparison with the energies of corresponding structures for $SiF_3(CO)_2^+$ is shown in Figure 8. The molecular orbital calculations show the lowest energy isomer, structure **7**, to have two equivalent CO molecules, both attached through carbon, and to have C$-$O distances (1.964 Å) shorter than those found in the other adducts. In **7** the bond angles of 103.9° for angle FSiC and 125.9° for CSiC deviate significantly from those expected for a tetrahedral arrangement and the structure is clearly distorted toward being a trigonal bipyramid in which the two CO ligands occupy the axial

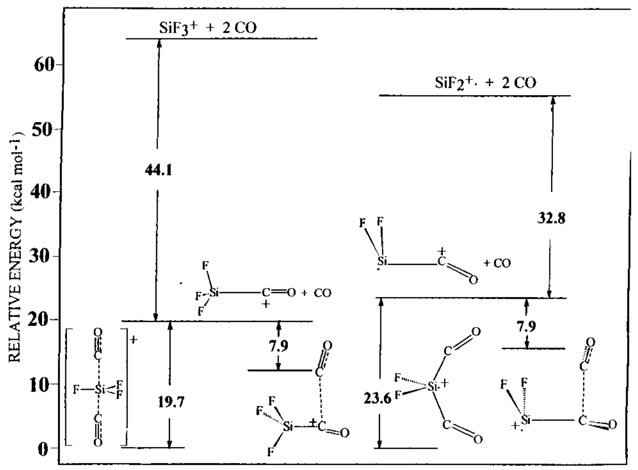

Figure 8. Comparison of the computed energies of selected isomers of $SiF_3(CO)_2^+$ and $SiF_2(CO)_2^{\bullet+}$. Relative energies are in kcal mol^{-1}.

positions and the two fluorine atoms and the unpaired electron are in the three equatorial positions. The solvated ion **8** in which CO is attached to ion **5** through carbon has a long C−C distance (2.718 Å) and is at a minimum of 15.7 kcal mol^{-1} above ion **7**. There is little evidence in the CID results shown in Figure 3 for the formation of more than one isomer of $SiF_2(CO)_2^{\bullet+}$ in the reaction of $SiF_2(CO)^{\bullet+}$ with CO, but isomers would not be resolved if their dissociation thresholds were too similar.

Conclusions

The parent silonium ion, SiH_5^+, has previously been shown to be a silenium ion, SiH_3^+, solvated by a hydrogen molecule. On this potential energy surface the five-coordinate structure with D_{3h} symmetry for SiH_5^+ is at high energy and is a high-order saddle point. Our discovery that the gas-phase reactions of $SiF_2^{\bullet+}$ and SiF_3^+ with CO yield, as final products, ions of the empirical formulas $SiF_2(CO)_2^{\bullet+}$ and $SiF_3(CO)_2^+$, with the latter having at least three different structural isomers, prompted us to investigate the structures of these ions using DFT molecular orbital calculations. The structure of the ion at the global minimum on the $SiF_3(CO)_2^+$ potential energy surface was found to contain a pentacoordinate Si, with the three F atoms in the equatorial positions and the two CO molecules loosely bound in the axial positions. The lowest energy isomer on the $SiF_2(CO)_2^{\bullet+}$ potential energy surface has a structure that is between a tetrahedral arrangement and a five-coordinate arrangement in which the two F atoms and the unpaired electron are in equatorial positions and the two CO molecules again are axial. Preliminary low-level calculations with a variety of substituents on $SiX_3Y_2^+$ showed that generally when F atoms are in the equatorial positions, Si has a tendency to become pentacoordinate.[32] For example, on the $SiF_3(NH_3)_2^+$ potential energy surface the trigonal bipyramidal structure with the three F atoms in the equatorial positions is 10.6 kcal mol^{-1} lower than the solvated tetrahedral ion $SiF_3(NH_3)^+\cdots NH_3$. This energy difference is smaller than that for **3**, despite the presence of a much stronger ligand in the axial position. It appears then that the combination of F, an element that forms a very strong bond with Si, and CO, a molecule that forms a relatively weak bond with Si, is ideal for the formation of a five-coordinate silonium ion.

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