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Theoretical and experimental studies of F_3SiCO^+ and F_3SiOC^+

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Abstract

Density-functional molecular orbital calculations and multi-collision-induced dissociation (CID) experiments in the gas phase have been performed on isomers associated formally with the addition of CO to SiF_3^+. Calculations at the B-LYP/6-31G(d,p) level of theory show that the isomer F_3SiCO^+ has an energy lower than that of F_3SiOC^+ by 17.8 kcal mol^{-1}, and thus establish that the potential energy surface for these ions is similar to those for the analogous H_3SiCO^+ and $(CH_3)_3SiCO^+$ ions in this respect. The transition structure for the interconversion of F_3SiCO^+ and F_3SiOC^+ is 7.5 kcal mol^{-1} in energy below that of dissociated $SiF_3^+ + CO$, a situation which is similar qualitatively to that for H_3SiCO^+, but differs qualitatively from that for $(CH_3)_3SiCO^+$. The calculations also indicate that the isomerization of F_3SiCO^+ to F_3SiOC^+ requires 35.0 kcal mol^{-1}. Multi-collision CID experiments performed with a selected-ion flow tube (SIFT) apparatus suggest that both F_3SiCO^+ and F_3SiOC^+ are produced by the reaction of SiF_3^+ with CO in an abundance ratio of approximately 0.85 : 0.15, and are stable in the gas phase.

Keywords: Density-functional theory; F_3SiCO^+ structures and stabilities; Gas-phase ion chemistry; Multi-collision CID; selected-ion flow tube (SIFT)

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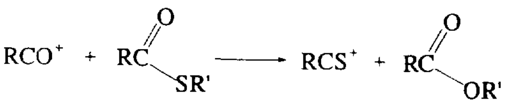
1. Introduction

The chemistry of acetyl cations with the formulae XCH_2CO^+ (where $X = H$, F, OH, NH_2, CH_3) has received considerable experimental and theoretical attention in recent years. Such species, historically, have been of interest in solution chemistry as reaction intermediates in Friedel–Crafts acylations [1] as well as in decarbonylation reactions of carboxylic acids in concentrated mineral acids [2].

Acetyl cations also have been investigated widely in gas-phase reactions [3,4]. Species of the formulae RCO^+ ($R = CH_3$, CH_3CH_2) have been found to react with sulfur analogues of carboxylic acids and esters to form thioacylium cations, as shown in Eq. (1):



$$RCO^+ + RC(=O)SR' \longrightarrow RCS^+ + RC(=O)OR' \quad (1)$$

Subsequent ab initio molecular orbital calculations have identified the thioacetyl cation $RC{=}S^+$ ($R = CH_3$) as existing at the global minimum on its potential energy surface [5]. Similar theoretical studies of XCH_2CO^+ isomers have shown the analogous cations (i.e. $X{-}CH_2{-}C{=}O^+$ species) to exist at the

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respective global minima for X = H [6,7], CH_3, OH, and F [7]. In addition, similar results have been found from ab initio investigations of the surface for which X = H and for which the β-carbon is replaced by silicon (i.e. H_3SiCO^+) [7,8], as well as for its trimethyl analogue, $(CH_3)_3SiCO^+$ [8]. Theoretical studies of the interconversion of the R_3SiCO^+ and R_3SiOC^+ isomers suggest that, both for R = H and for R = CH_3, the respective transition structures lie very close in energy to that of the dissociated species $R_3Si^+ + CO$ [8]. These results raise questions regarding the feasibility of the interconversions of these two sets of isomers without causing dissociation.

In recent years, considerable experimental effort also has been expended on the studies of "Lewis superacids" such as CF_3^+ and SiF_3^+ in the gas phase. In particular, such species have been reacted with neutral molecules such as CH_3OH, CH_3CH_2OH, and CH_3NH_2, in attempts to produce long-lived primary cations such as CH_3^+ and $CH_3CH_2^+$, as well as with other Lewis bases such as H_2O and NH_3 [9]. To our knowledge, however, there have been no attempts to form acylium ions by reaction of SiF_3^+ with carbon monoxide. Formally, CO contains lone electron pairs on both of its constituent atoms, and SiF_3^+ contains an empty p-orbital on the positively charged silicon atom. An a priori consideration of these species, then, suggests the likelihood of reaction at the silicon centre, either with carbon or with oxygen. Here, we present the results of our theoretical and experimental investigations of the reaction of the trifluorosilyl cation SiF_3^+ with carbon monoxide.

2. Computational methods

Theoretical calculations have been performed with the GAUSSIAN suite of programs [10]. Geometric optimizations of all minima and first-order saddle points have been carried out with the density-functional [11] Becke technique which includes the Slater (local spin density) exchange functional [11(a),11(b),12] with non-local gradient-corrected terms included [13] and the Lee–Yang–Parr method which includes local and non-local gradient-corrected correlation functionals [14]. Geometry optimizations and subsequent harmonic frequency calculations at this level of theory (henceforth denoted B-LYP) were performed using the standard Gaussian split-valence 6-31G(d,p) basis set [15]. The transition structures were located by an initial crude point-by-point profile analysis, followed by refinement with the eigenvector-following (EF) algorithm [16]. Intrinsic reaction coordinate (IRC) analyses [17] were performed to verify the identities of the two species at local minima which are interconverted through the transition structures. In addition, counterpoise calculations were performed on the optimized transition structure geometries at the same level of theory in an effort to assess the effects of basis set superposition error (BSSE) on the total electronic energies of the dissociation products on the surfaces under study [18].

3. Experimental methods

The addition of CO to SiF_3^+ was achieved in the selected-ion flow tube (SIFT) apparatus in the Ion Chemistry Laboratory at York University [19,20]. The production of SiF_3^+ ions was achieved by electron impact upon neutral SiF_4 (99.99% minimum purity, supplied by Matheson Gas Products, Whitby, Ont. at 50 eV. These 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 Torr. The helium buffer gas was initially passed through zeolite traps cooled to liquid nitrogen temperatures in order to remove water vapour

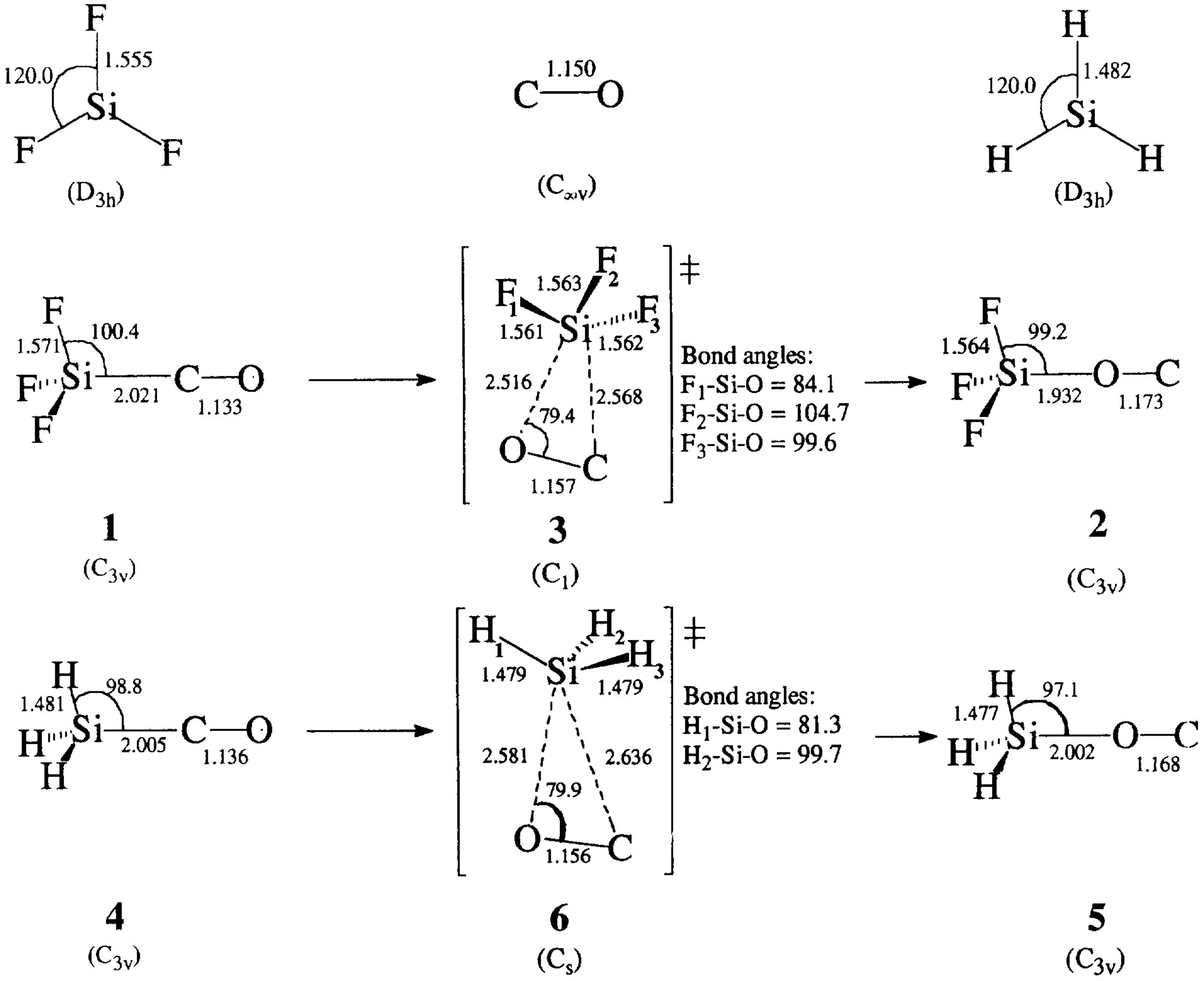


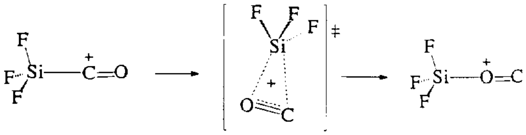
Fig. 1. Structural parameters associated with cations SiF_3^+, SiH_3^+, **1**, **2**, **4**, **5**, transition structures **3**, **6**, and neutral CO, as calculated a B-LYP/6-31G(d,p). Bond lengths are in ångstrøms, and bond angles in degrees.

and then used without further purification. The gaseous carbon monoxide used in the reaction also was of high purity (99.5% min.; Matheson). A recent modification of the SIFT apparatus at York University has allowed the subsequent analyses of product ions using a multi-collision-induced dissociation (CID) technique, described in detail elsewhere [21,22]. Briefly, CID is achieved by biasing the downstream sampling nose cone in the SIFT apparatus with respect to the flow tube by voltages in the range from 0 to −80 V. These experiments are performed in helium or in argon at ambient pressures in the range of 0.35 ± 0.02 Torr. Such investigations, then, in principle, can be used to distinguish between structural isomers of a given molecular formula on the basis of differences in the resulting CID spectra.

4. Results and discussion

4.1. Theoretical results

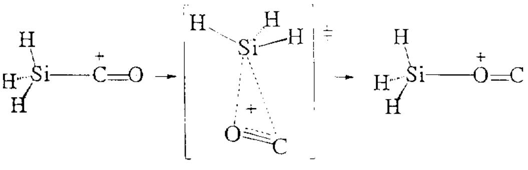
We have performed theoretical calculations on the two isomers (**1** and **2**) which may, in principle, be associated with the gas-phase addition of SiF_3^+ and CO, as well as the transition structure to their interconversion (**3**) as is shown in Eq. (2):



(2)

1 3 2

For the purpose of comparison with the previously studied SiH_3CO^+ surface [7,8], we have also performed theoretical calculations at the same level of theory on the three structures **4**, **5**, and **6** shown in Eq. (3), which are analogous to ions **1**, **2**, and **3** respectively:

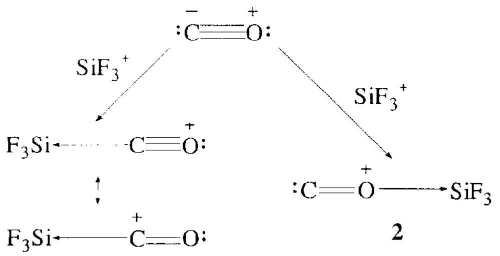


(3)

4 6 5

The geometric parameters optimized for these structures are given in Fig. 1. The total electronic energies, zero-point vibrational energies (ZPE), and relative energies (with ZPE included) are given in Table 1. The critical points of these two potential energy surfaces, as well as the relative energies of the respective dissociation products, are shown in Fig. 2.

The Si–C distance in **1** (2.021 Å) is considerably longer than that found in silaethane (1.867 Å) [23], whereas the carbon-oxygen separation (1.133 Å) actually is slightly shorter than that calculated for a CO molecule in isolation at this level of theory (1.150 Å). This result suggests that the carbon–oxygen bonding is strengthened slightly on interaction with the electrophile SiF_3^+. By contrast, ion **2** contains a longer carbon–oxygen bond (1.173 Å) than that calculated for CO in isolation, suggesting a weakening of the carbon–oxygen bonding upon interaction with SiF_3^+. This apparent contradiction can be explained as follows:



1 2

In producing structure **2** from SiF_3^+ and CO, the electron density on the oxygen atom of the CO moiety is depleted by the formal donation of its lone electron pair to the empty p-orbital on the silicon atom of SiF_3^+. This interaction increases the positive charge on the oxygen atom and results in electron withdrawal from the multiple CO bond to oxygen. Hence the carbon–oxygen separation in **2** is greater than that calculated for neutral CO. By contrast, in the formation of ion **1**, the carbon atom of CO donates an electron pair to the formally empty p-orbital on the silicon atom of SiF_3^+. This donation depletes the electron density around the carbon atom, thereby removing the surplus negative charge and enhancing the π-donation from oxygen. Thus the carbon–oxygen distance in **1** is shorter than that of neutral carbon monoxide. These differences in CO bonding are illustrated clearly by the Mayer bond indices [24], calculated at HF/6-31G(d,p)//B-LYP/6-31G(d,p), and shown in Fig. 3.

Table 1
Total electronic[a] and relative energies[b] of F_3SiCO^+ and H_3SiCO^+ isomers at B-LYP/6-31G(d,p)

Ion	Total energy[a]	ZPE[c]	Relative energy with respect to **1** (ZPE included)
1	−702.14055	10.7	0.0
2	−702.11096	9.96	+17.8
3	−702.08235	9.26	+35.0
$SiF_3^+ + CO$	−702.06708	8.77	+44.1 (+42.5)[e]
4	−404.26756	19.5	0.0[d]
5	−404.23552	18.9	+19.5[d]
6	−404.21331	18.0	+32.5[d]
$SiH_3^+ + CO$	−404.20056	16.5	+39.1[d] (+37.7)[e]

[a] In hartrees.
[b] In kcal mol^{-1}.
[c] From frequency calculations on optimized structures at B-LYP/6-31G(d,p); unscaled.
[d] Relative energy with respect to **4**, ZPE included, in kcal mol^{-1}.
[e] Values in parentheses include corrections for BSSE.

Many of the structural changes accompanying addition of CO to SiH_3^+ are similar to those found in the adducts of SiF_3^+. However, there are some pronounced differences in the bonding between silicon and fluorine in ions **1**, **2**, and isolated SiF_3^+, when compared with that between silicon and hydrogen in ions **4**, **5**, and isolated SiH_3^+. The Mayer indices for

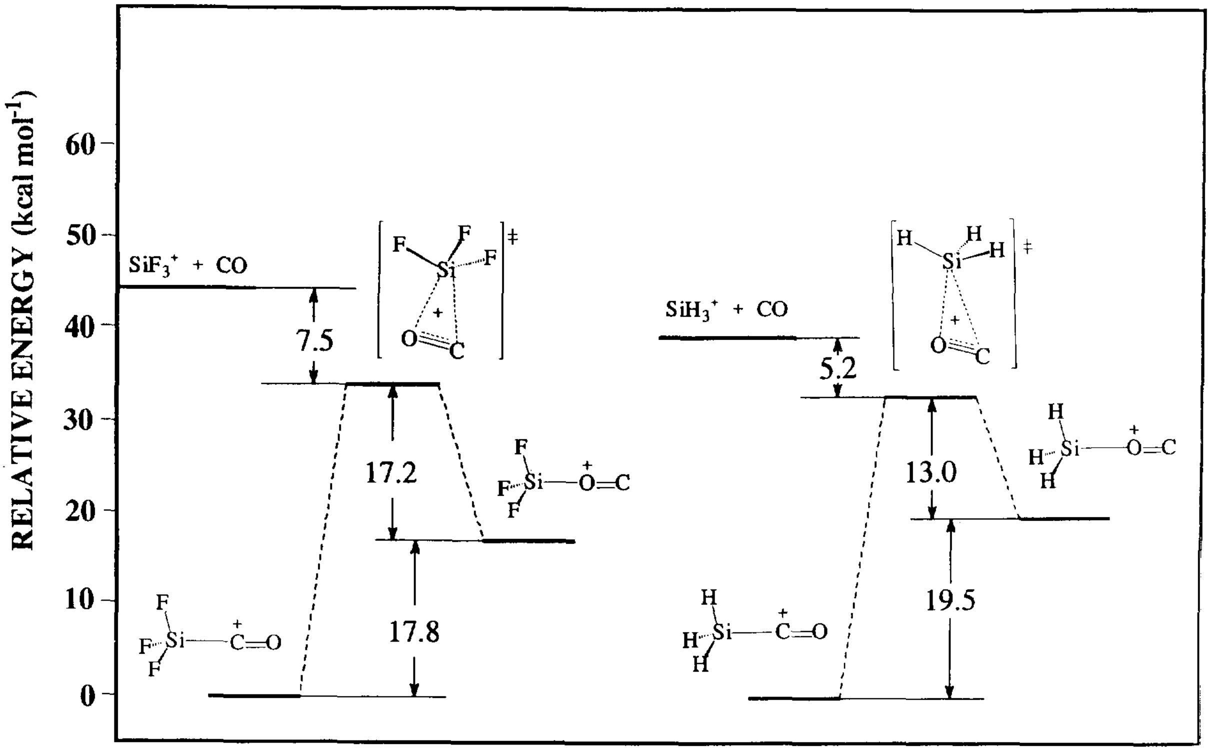


Fig. 2. Critical points on the F_3SiCO^+ and H_3SiCO^+ potential energy hypersurfaces, as well as dissociated $SiF_3^+ + CO$, and dissociated $SiH_3^+ + CO$, as calculated at B-LYP/6-31G(d,p).

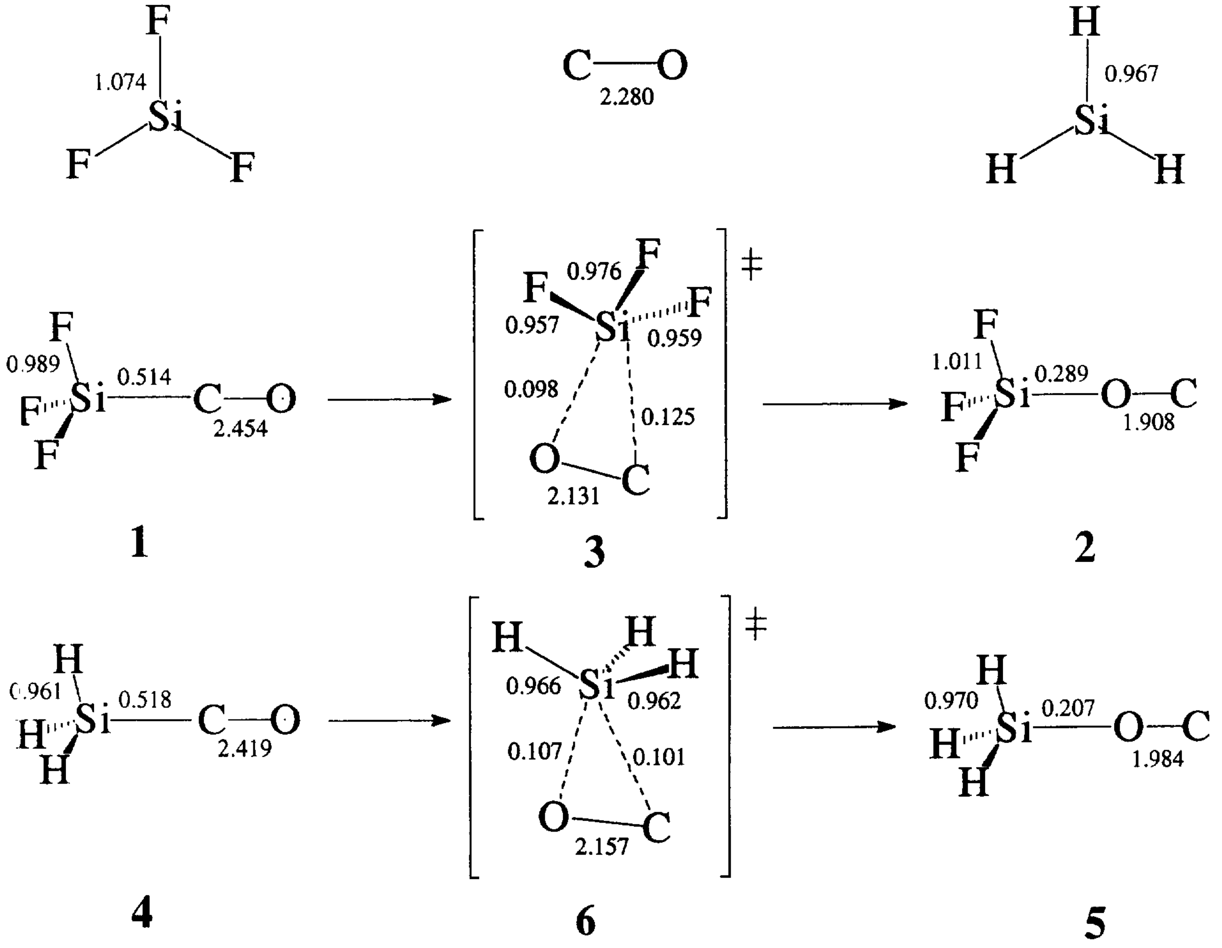


Fig. 3. Mayer bond indices of optimized cations SiF_3^+, SiH_3^+, **1**, **2**, **4**, and **5**, transition structures **3** and **6**, and neutral CO, as calculated at HF/6-31G(d,p)//B-LYP/6-31G(d,p).

Si–H bonds in isolated SiH_3^+ and in adducts **4** and **5** are similar in magnitude (0.967, 0.961, and 0.970, respectively); thus Si–H bonding is not perturbed severely in the SiH_3^+ moiety on addition to either end of a CO molecule. By contrast, the Si–F bonding in the analogous trifluorinated ions changes more noticeably on proceeding from isolated SiF_3^+ to ions **1** and **2** (Mayer bond indices for the Si–F bonds of these species are 1.074, 0.989, and 1.011, respectively). These decreases in Mayer bond order are accompanied by increases in these bond lengths, from 1.555 Å in SiF_3^+ to 1.571 Å in **1** and 1.564 Å in **2**. Clearly, a greater amount of electron density is withdrawn from the Si–F bonds on formation of **1** and **2** than is the case for the Si–H bonds in the trihydrogen analogues. These results are manifestations of the existence of partial double bonding in SiF_3^+ (via F → Si back-donation of π electrons) and the lack of such bonding in SiH_3^+.

In the adduct ions, the calculated F–Si–C and H–Si–C bond angles are 100° or smaller. Thus this feature of the product ion geometries lies between that of a tetrahedral geometry (angle 109.47°) and a planar geometry (angle 90°). For example, the carbon analogue of **1**, H_3CCO^+, has been calculated to possess an H–C–C bond angle of 107.7° [7], a value which is very different from the H–Si–C bond angle of **1** (98.8°). These results suggest that the SiF_3^+ and SiH_3^+ moieties have much less severely perturbed geometries (vis-à-vis isolated SiF_3^+ and SiH_3^+, respectively) throughout the interconversion processes depicted in Eqs. (2) and (3) than is the case for analogous acylium ions. This phenomenon can be attributed to the weaker overlap between orbitals of second-row silicon and first-row carbon or oxygen than exists between carbon and carbon, or between carbon and oxygen [8].

In addition, these calculations indicate that Si–O bonding in **2** (bond order 0.289) is weaker than Si–C bonding in **1** (bond order 0.514). Isomer **1** is calculated to be lower in energy than **2** by 17.8 kcal mol^{-1}. Similarly, the more stable isomer on the H_3SiCO^+ surface, **4**, involves Si–C bonding [7,8]. In this respect, the F_3SiCO^+ surface is similar to those of the previously reported trihydrogen [7,8] and analogous trimethyl [8] cations, as well as to those of most XH_2CCO^+ ions; the more stable isomer contains CO bonding to the reactant cation through carbon, rather than through oxygen.

The energetics of the H_3SiCO^+ and F_3SiCO^+ surfaces, as shown in Fig. 2, reveal a considerable difference in the basicity of the carbon atom of CO vis-à-vis that of the oxygen atom. With SiF_3^+ as a Lewis acid, there is a greater binding energy associated with the formation of **1** (42.5 kcal mol^{-1}) than with formation of **2** (24.7 kcal mol^{-1}). Thus the carbon atom of CO is more basic than the oxygen atom by 17.8 kcal mol^{-1}. Similarly, with SiH_3^+ as the Lewis acid, the binding energies of ions **4** and **5** are 37.7 kcal mol^{-1} and 18.2 kcal mol^{-1}, respectively (a difference of 19.5 kcal mol^{-1}).

The relative energies of the dissociation products have been calculated with the inclusion of estimated BSSEs obtained by the performance of counterpoise calculations [18]. Such corrections lower the energy of separated $SiF_3^+ + CO$ by 1.6 kcal mol^{-1}, and lower that of dissociated $SiH_3^+ + CO$ by 1.4 kcal mol^{-1}. These corrections are similar in magnitude to the value of 1.9 kcal mol^{-1} reported in a previous theoretical study of H_3SiCO^+ [8]; the small difference in values can be attributed to differences in the basis set used in the respective analyses. It should be noted that the basicities of carbon and oxygen in CO as reported in the preceding paragraph include these BSSE correction terms.

Inclusion of BSSE also is of importance in determining the relative energy of a given transition structure vis-à-vis its dissociation products. Clearly, if the transition structure lies above the dissociated products in energy, isomerization without fragmentation and subsequent recombination cannot occur. If the transition structure energy is below that of the dissociation products, isomerization is possible (at least in principle). In the case of the previously studied R_3SiCO^+ surfaces, the transition structure for the isomerization of R_3SiCO^+ to R_3SiOC^+ has been found to be above the dissociation limit for $R = CH_3$ [8], and below this limit for $R = H$ [8]. Our calculated results at B-LYP/6-31G(d,p) show that the transition structures for both the F_3SiCO^+ and the H_3SiCO^+ surface lie below the respective dissociation products in energy.

With respect to the magnitudes of the energy differences between the transition structures and the dissociation limits, our calculated results have yielded values of 7.5 kcal mol^{-1} for F_3SiCO^+ and 5.2 kcal mol^{-1} for H_3SiCO^+ (with both ZPE and BSSE corrections included). This last result is in good agreement with that obtained in previous studies at the MP4/6-311G(2df,2pd)//MP2/6-31G(d) level of theory (3.5 kcal mol^{-1}) [8] and, in this regard, instills confidence in the reliability of our method of obtaining relative energies for such species by using B-LYP-level calculations.

The isomerization of **2** to **1** on the F_3SiCO^+

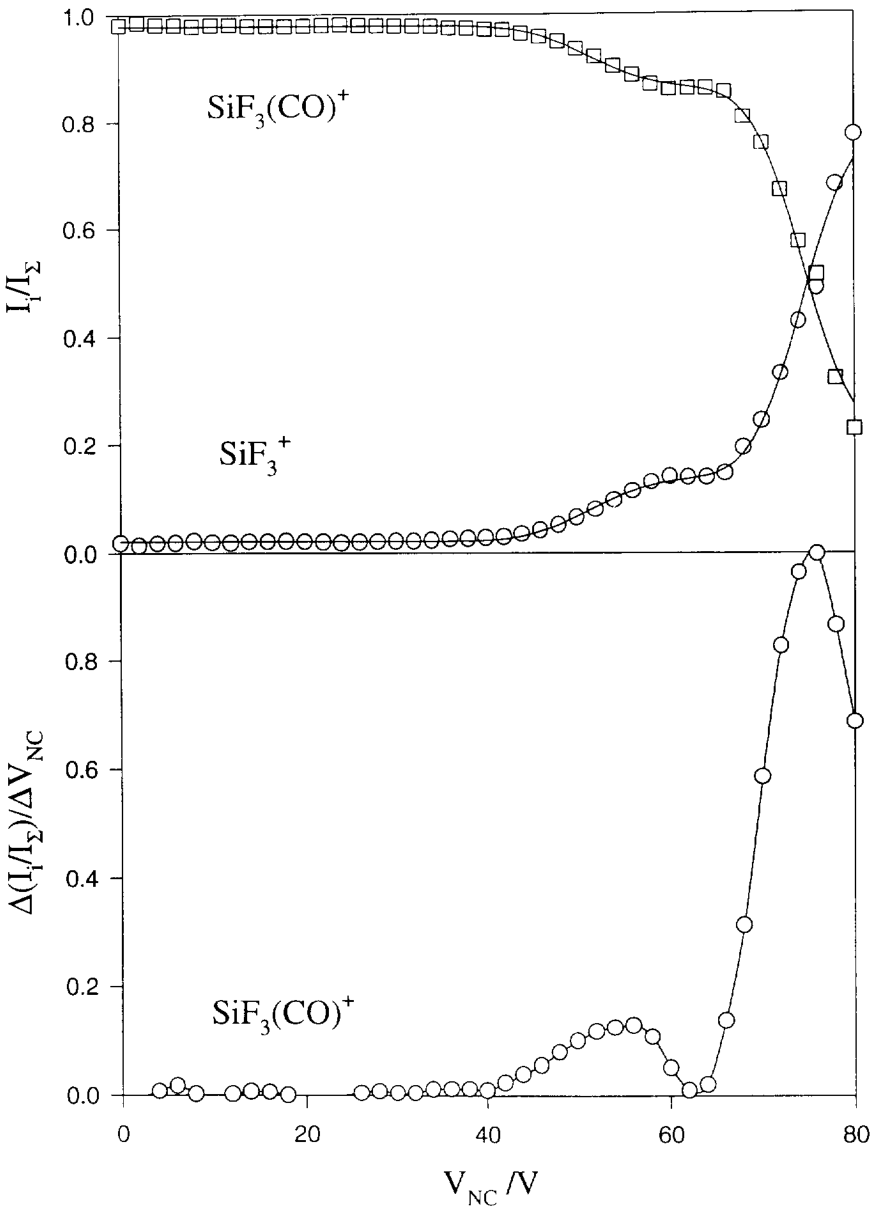


Fig. 4. CID spectrum of F_3SiCO^+ in helium buffer gas. Top: (ion signal intensity vs. nose-cone voltage). Bottom: first derivative of ion signal intensity with respect to nose-cone voltage multiplied by (−1) vs. nose-cone voltage.

surface, through transition structure **3**, requires 17.2 kcal mol^{-1} of energy. The corresponding value for the isomerization of **5** to **4**, through **6**, on the analogous trihydrogen surface is 13.0 kcal mol^{-1}, a result which, again, is similar to that previously obtained at MP4/6-311G(2df,2pd)//MP2/6-31G(d) (12.4 kcal mol^{-1}) [8]. Isomerization of $(CH_3)_3SiOC^+$ to $(CH_3)_3SiCO^+$ requires that an even smaller barrier be overcome (6.6 kcal mol^{-1}). Qualitatively, then, the observed trend in magnitudes of isomerization barriers for R_3SiCO^+ ions is $R = F > H > CH_3$. This trend in isomerization barriers can be compared with that of carbon and oxygen basicities on CO, for which nucleophilic attack on SiR_3^+ species also follows the order $R = F > H > CH_3$. Since these trends are valid for carbon basicity (as in ions **1** and **4**), for oxygen basicity (as in ions **2** and **5**), and for π basicity (as in transition structures **3** and **6**), then clearly formation of each of these types of complex gives the same order of Lewis acidities for the silyl cations, $SiF_3^+ > SiH_3^+ > Si(CH_3)_3^+$. This trend also is consistent with that of the ionization energies (IEs) of associated neutral radicals $SiF_3\cdot$ (IE = 9.3 ± 0.5 eV), $SiH_3\cdot$ (IE = 8.14 ± 0.01 eV), and $Si(CH_3)_3\cdot$ (IE = 6.5 ± 0.5 eV) [25].

4.2. Experimental results

Product ions of *m/z* 113 (which correspond to the molecular formula SiF_3CO^+) were produced as adducts of the gas-phase reaction of SiF_3^+ with CO. The effective bimolecular rate coefficient k for this reaction was measured to be $(4.1 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at a pressure of 0.35 ± 0.01 Torr of helium.

A multi-collision CID analysis was performed on the product ions at *m/z* 113 in separate experiments. A typical CID spectrum of ion signal intensities versus nose-cone voltage (V_{NC}), along with the negative of the first derivative of the ion signal with respect to V_{NC} versus V_{NC} is shown in Fig. 4. Fig. 4 (top) shows that the ion signal intensity associated with *m/z* 113 is fairly constant at nose-cone voltages of 0.0 to approximately −42 V. Beyond −42 V this ion signal drops to approximately 0.85 of its original intensity, accompanied by an increase in the ion signal at *m/z* 85. These two ion signal intensities remain fairly constant up to $V_{NC} = -65$ V, beyond which a large second decrease in the *m/z* 113 ion signal and a corresponding large second increase in the *m/z* 85 ion signal intensity can be observed. These changes in ion signal intensity are even more evident on observing the differential spectrum (Fig. 4, bottom) in which the two changes in the *m/z* 113 signal appear as two peaks in the differential curve. They are consistent with the dissociation of two isomeric ions at *m/z* 113 into an ion with *m/z* 85 and a neutral product.

Our theoretical calculations have shown that two isomers are possible for the adduct of SiF_3^+ and CO (**1** and **2**). Fig. 3 shows that the Si–C interaction in **1** and the Si–O interaction in **2** do not correspond to full formal bonds and therefore it is probable that dissociations of these ions by CID occur by breaking these partial bonds. Such dissociations, however, would result in the formation of identical product fragments, $SiF_3^+ + CO$. In this regard a distinction between **1** and **2** using the dissociation products would not be possible. However, as Si–C and Si–O bonds do not have the same energy (an average formal Si–C bond energy is approximately 72 kcal mol^{-1}; that of Si–O is about 108 kcal mol^{-1}) [26], and, further, as the Mayer bond analyses of **1** and **2** have shown different amounts of bonding to CO depending upon whether attachment occurs to C or to O, it is highly likely that these two ions would dissociate at different applied nose-cone voltages under CID conditions.

We interpret our CID results as indicating that both ion **1** and ion **2** are produced from the reaction of SiF_3^+ with CO under our SIFT conditions, and that the abundance ratio of ion **1** to ion **2** under these conditions is approximately 0.85:0.15 at the point of ion sampling. The less stable $F_3Si{-}OC^+$ isomer **2** is expected to dissociate first, with the more stable $F_3Si{-}CO^+$ isomer **1** dissociating at higher nose-cone voltages. It is interesting to note that the ratio of the onset voltages, (−42 V)/(−65 V) = 0.65, is approximately equal to the ratio of the energies of the bonds dissociated, (24.7 kcal mol^{-1})/(42.5 kcal mol^{-1}) = 0.58.

Although the theory of our new CID technique is not yet fully developed, this result is not surprising given that the similarities in the mass and degrees of freedom of the isomeric ions being dissociated should lead to similar efficiencies in energy transfer.

The relative abundance of the two isomers measured at the point of sampling needs to be rationalized in terms of the kinetics of their formation by the addition of CO to SiF_3^+ and in terms of their subsequent conversion by isomerization. Clearly, the observed abundance ratio is *not* equal to an equilibrium distribution. The difference in the standard Gibbs free energies of formation between the two isomers yields an equilibrium constant of approximately 10^{-13}, i.e. in an equilibrium mixture of species **1** and **2**, almost all ions would have the structure of **1**. It is the large energy barrier for the interconversion of isomers **1** and **2** which prevents the achievement of equilibrium in the few milliseconds available in the reaction region prior to sampling.

The abundance ratio of the two isomers established initially by the addition reaction of SiF_3^+ with CO will be determined in part by collision dynamics. Ion–dipole and induced-dipole interaction will favour F_3Si^+–CO bond interaction and so the formation of isomer **1**. However, since the transition structure for the interconversion of **1** to **2** lies below the initial energy of the reactants SiF_3^+ and CO (see Fig. 2), isomerization by CO rotation is possible prior to collisional stabilization. The deeper potential energy well associated with isomer **1** will lead to a longer lifetime compared with its dissociation back to reactants and so to more favourable collisional stabilization of this isomer.

5. Conclusions

Density-functional theoretical calculations have been performed on the two isomers each of molecular formulae F_3SiCO^+ and H_3SiCO^+, which are associated with the additions of SiF_3^+ and SiH_3^+ to carbon monoxide in the gas phase, as well as on the transition structures to their respective interconversions. On both surfaces, the isomer in which silicon is bonded to carbon (F_3SiCO^+ and H_3SiCO^+) has been found to be the lower energy isomer. The transition structures for the interconversions between minima on both surfaces lie below the energies of the dissociation products, topological features which are unlike those on the $(CH_3)_3SiCO^+$ surface [8]. The similarities of the results obtained on the H_3SiCO^+ surface from our density-functional calculations and those obtained previously from Møller–Plesset theory [8] instill confidence in the reliability of using such density-functional methods to obtain information regarding relative energies of isomers on a given potential energy hypersurface as well as to obtain insight into binding energies of constituent ions and isomerization energies. The results of SIFT-CID experiments indicate that both the isomers F_3SiCO^+ and F_3SiOC^+ exist as stable species in the gas phase. The experimental confirmation of the theoretical predictions provides an excellent illustration of the complementary nature of these two types of study in yielding insight into the properties of ions in the gas phase.

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