

# Gas-phase ion chemistry and ion thermochemistry of phenyltrifluorosilane

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## Abstract

The ion/molecule reactions of phenyltrifluorosilane with  $F^-$ ,  $CH_3O^-$  and  $OH^-$  and the thermochemical properties of the resulting ions were investigated by using a flowing afterglow—triple quadrupole mass spectrometer. The silane reacts with fluoride and methoxide ions by addition, whereas the reaction with hydroxide proceeds by addition and loss of HF to form the phenyldifluorosiloxide ion. Collision-induced dissociation (CID) of the adduct ions produces predominantly phenide ion, although rearrangement processes are also observed for the methoxide adduct. CID of the siloxide ion results in direct cleavage to form the  $SiF_2O^-$  ion, in addition to products formed by rearrangement. We also report the formation of the hydroxide adduct of phenyltrifluorosilane, and provide the first confirmation that activated hydroxide adducts of silanes dissociate by loss of RH. The hydride adduct of phenyltrifluorosilane is generated indirectly by the addition of fluoride to phenyldifluorosilane. Bond dissociation energies and rearrangement barriers were obtained for all ions from the energy-resolved CID cross sections. From the measured bond dissociation energies, the fluoride, hydride and methoxide affinities of phenyltrifluorosilane are determined to be  $79.4 \pm 3.3$  and  $64.0 \pm 3.2$ , and  $76.6 \pm 5.9$  kcal/mol, respectively, and the fluoride affinity of phenyldifluorosilane is found to be  $72.3 \pm 4.4$  kcal/mol. The hydride affinity (HA) of phenyltrifluorosilane is comparable to that of borane, suggesting that  $C_6H_5SiHF_3^-$  is a potential hydride reducing agent in the condensed phase.

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**Keywords:** Gas-phase ion chemistry; Ion thermochemistry; Phenyltrifluorosilane; Energy-resolved MS; CID

## 1. Introduction

It is well known that third row and lower main-group elements (e.g., P, S, Cl) can exhibit hypervalent behavior [1]. Silicon, in particular, is known to form pentavalent ions in solution, and representative examples have been isolated and characterized by NMR, IR, and X-ray crystallography [2–6]. Pentavalent siliconates are also readily prepared in the gas-phase

[7]. The unsubstituted ion,  $SiH_5^-$ , and alkyl substituted siliconates have been prepared by the reaction of silanes with hydride ions or other hydride donors [8,9]. Squires and co-workers have utilized alkoxy-silicate ions in studies of the hydride reductions of organic substrates [9–11]. Moreover, a wide variety of siliconates can be prepared by addition of nucleophilic ions to silanes, and Damrauer and co-workers have reported the formation of a variety of substituted siliconate ions [12,13]. However, little is known about the thermochemical properties of pentavalent siliconate ions and how they are affected by substi-

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tution [14]. In conjunction with their reactivity studies, Squires and co-workers have measured the hydride affinities of silane and alkylated derivatives [8,9]. Chloride and fluoride affinities have also been reported for silane and methylated silanes [15–17]. There have been few reports of more highly substituted siliconate ions or their thermochemical properties. In this work, we describe the ion/molecule reactivity of phenyltrifluorosilane and the thermochemical properties of negative ions derived from it. Phenyltrifluorosilane was selected for these studies because it is known to form a long-lived pentavalent siliconate ion,  $C_6H_5SiF_4^-$ , in solution upon reaction with fluoride ion [2,4,5,18–20]. The X-ray diffraction crystal structure of  $C_6H_5SiF_4^-$  clearly shows a pseudo-trigonal bipyramidal structure of the pentacoordinate system [21]. We show that the fluoride adduct can also be readily generated in the gas phase by the reaction of the silane with fluoride ion. We also report the formation of the hydride, hydroxide, and methoxide adducts of  $C_6H_5SiF_3$ , and the reaction with hydroxide ion. Lastly, energy resolved CID of the products has been used to determine the fluoride and hydride affinities of the silane and the bond dissociation energies in the ionic reaction products.

## 2. Experimental

### 2.1. Instrumental description and data analysis

All gas-phase ion/molecule reactions were carried out using a flowing afterglow—triple quadrupole mass spectrometer that has been described previously [22,23]. Primary ionic reagents were prepared by 70 eV electron ionization (EI) of neutral precursors and carried by helium buffer gas (0.400 torr, flow(He) = 190 STP  $cm^3/s$ ) through the flow tube, where they were allowed to react with silane added through micrometering valves. Fluoride ion was produced by EI of fluorine gas, while hydroxide ion was prepared by EI of a mixture of methane and nitrous oxide (2:1 ratio). Methoxide ion was prepared by proton transfer from methanol to hydroxide ion. Ions

generated in the flow tube were sampled through a 1 mm nose cone orifice into a differentially pumped region, where they are analyzed by using a triple quadrupole mass filter (EXTREL). Collision-induced dissociation (CID) is carried out by mass selecting the parent ion of interest with the first quadrupole and injecting the ion into the second quadrupole, which serves as a gas-tight collision cell containing argon as the target gas. The CID collision energy is controlled by the pole offset voltage, and the absolute energy origin is established by using retarding potential analysis. The uncertainty in the absolute energy scale is estimated to be  $\pm 0.15$  eV in the laboratory frame. Product ions are mass analyzed with the third quadrupole and detected with a channeltron particle detector operated in pulsed-counting mode. Cross sections for CID,  $\sigma$ , are calculated using  $I/I_0 = \sigma Nl$ , where  $I$  and  $I_0$  are the intensities of the product and reactant ions, respectively,  $N$  is the number density of the target, and  $l$  is the effective collision path length, calibrated to be  $24 \pm 4$  cm [23] by using the reaction of  $Ar^+ + D_2$ , which has a well-established cross section [24]. Cross sections are measured as a function of target pressure and extrapolated to zero pressure, single collision conditions. Cross sections are modeled with the exponential expression shown in Eq. (1) [25–28], where  $E$  is the center-of-mass collision energy of the parent ion,  $g_i$  is the fraction of the ions with internal energy  $E_i$ ,  $E_0$  is the threshold energy for dissociation,  $n$  is a parameter that reflects the energy deposition in the collision [29], and  $\sigma_0$  is a scaling factor. The data are modeled by adjusting the parameters to correspond with the steeply rising portion of the appearance curve(s) directly past the threshold. Also convoluted into the fit are the ion kinetic energy distributions, approximated as a Gaussian with a 1.5 eV (laboratory frame) full-width at half-maximum, and a Doppler broadening function to account for motion of the target. The factor  $P_i$  is the probability for ion dissociation, which is calculated from RRKM theory.

$$\sigma(E) = \frac{\sigma_0 \sum_i P_i g_i (E + E_i - E_0)^n}{E} \quad (1)$$

For direct dissociation reactions, a product-like transition state is assumed, corresponding to the phase-space limit [30]. Activation entropies for direct dissociation reactions are generally +10–20 cal/mol K, indicating loose transition states. The method of determining the properties of rearrangement transition states is described below. Data analysis and modeling were carried out using the CRUNCH 4D [30–34] software package. Threshold energies are 0 K  $\Delta E$  values and are converted to 298 K bond dissociation enthalpies by using the integrated heat capacities of reactants and products. Uncertainties in enthalpy values are calculated by statistical combination of the uncertainty in the absolute energy scale for the experiment (0.15 eV lab frame), the standard deviation of values obtained from replicate experimental trials, and uncertainty due to error in the transition state. Error in the transition state is estimated as the change in the threshold energy that results when the frequencies of the transition state are adjusted to change the activation entropy by  $\pm 2$  cal/mol K. Rotational constants and frequencies required to calculate the internal energies of the ion and the RRKM dissociation rates were calculated at the BLYP/6-31+G\* level of theory [35–37] using Gaussian 98 [38]. Optimized structures and calculated frequencies are provided as supplemental material at the author's website (<http://www.chem.purdue.edu/wenthold/publications.htm>).

## 2.2. Materials

Unless otherwise indicated, reagents were used as received without further purification. Fluorine gas (5% in helium) was purchased from Spectra Gases. Methane (99.5%) and nitrous oxide (99%) were obtained from BOC gases. Helium gas was purified via a liquid nitrogen trap containing molecular sieves. Methanol was obtained from Mallinckrodt. Phenyltrifluorosilane (Gelest), phenyltrichlorosilane (Aldrich), phenyltrimethylsilane (Aldrich), copper(I) iodide (Fisher), phenylsilane (Aldrich), and potassium fluoride (Aldrich) were used as received. Copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) (Baker) was decomposed in vacuo at 100 °C to remove water [39].

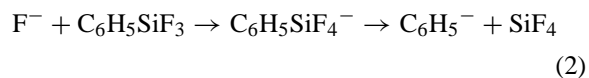
The dehydrated copper(II) chloride that resulted had a tan color, and was stored in a desiccator prior to use. Diethyl ether was dried and distilled under nitrogen over sodium and benzophenone. Phenyl-difluorosilane ( $\text{C}_6\text{H}_5\text{SiHF}_2$ ) was prepared from phenylsilane according to the procedures reported by Kunai et al. [40]. This preparation led to a mixture of polyfluorophenylsilanes, including phenyl-difluorosilane (~60%), phenyl-trifluorosilane (~30%), and very little of the monofluorinated silane present. This mixture was not purified further.

## 3. Results

The following sections describe the results of the studies of the ion/molecule reactivity of phenyltrifluorosilane. We describe observed reactivity of the silane with the primary reagent ions fluoride, methoxide, and hydroxide and discuss the collision-induced dissociation reactions of the product ions.

### 3.1. Reaction with fluoride

The sole product in the reaction of  $\text{C}_6\text{H}_5\text{SiF}_3$  with fluoride is the phenyltetrafluorosilicate ion,  $\text{C}_6\text{H}_5\text{SiF}_4^-$ , corresponding to the product previously observed in solution [2,18–20]. Upon CID, the gaseous ion loses  $\text{SiF}_4$  to give the phenyl anion as the only ionic product (Eq. (2)).



### 3.2. Reaction with methoxide

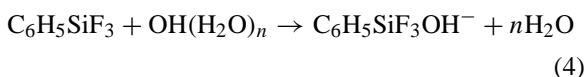
Adduct formation is also the only pathway observed for the reaction of phenyltrifluorosilane with methoxide. CID of the methoxide adduct,  $\text{C}_6\text{H}_5\text{SiF}_3\text{OCH}_3^-$ , proceeds by two pathways. The major fragmentation pathway yields phenide ion,  $\text{C}_6\text{H}_5^-$  and  $\text{SiF}_3\text{OCH}_3$ . A minor pathway gives formation of  $\text{SiF}_3\text{O}^-$  and toluene [41]. The formation of  $\text{SiF}_3\text{O}^-$  is not surprising as the ion is isoelectronic to  $\text{SiF}_4$ .

### 3.3. Reaction with hydroxide, $\text{OH}^-$

Reaction of phenyltrifluorosilane with hydroxide proceeds by addition of  $\text{OH}^-$  and subsequent loss of HF to form the phenyldifluorosiloxide ion,  $\text{C}_6\text{H}_5\text{SiF}_2\text{O}^-$ , as the sole ionic product (Eq. (3)). The reaction of  $\text{C}_6\text{H}_5\text{SiF}_3$  with hydroxide is similar to that observed for simple silanes and trimethylsilanes, which react by nucleophilic addition followed by loss of RH [7,12,41]. Upon CID, the  $\text{C}_6\text{H}_5\text{SiF}_2\text{O}^-$  ion fragments to give  $\text{SiF}_2\text{O}^-$  as the major product at high energies. Other products include  $\text{C}_6\text{H}_4\text{SiFO}^-$ , formed by loss of HF, and phenoxide, which is formed by loss of  $\text{SiF}_2$ . The products formed by rearrangement processes are more prevalent at low collision energies.



As has been proposed previously [7], the reaction to form the siloxide likely proceeds through a transient hydroxysiliconate ion. The hydroxide adduct of phenyltrifluorosilane can be prepared in abundance by the reaction (Eq. (4)) of  $\text{C}_6\text{H}_5\text{SiF}_3$  with solvated hydroxide ion,  $\text{OH}^-(\text{H}_2\text{O})_n$  [42,43]. The hydroxide adduct efficiently loses HF upon CID forming  $\text{C}_6\text{H}_5\text{SiF}_2\text{O}^-$  as the major ionic product. It also has a minor pathway with loss of benzene forming  $\text{SiF}_3\text{O}^-$ .



Hydroxide adducts have been observed previously for chloro-, fluoro-, and methoxytrimethylsilane [12]. The hydroxide adduct of methoxytrimethylsilane can be formed by a direct addition reaction, but only under the high pressure conditions of a flow reactor [44]. Halogenated hydroxysiliconates were prepared by addition of halide ions to trimethylsilanol (R. Damrauer, personal communication). This is the first instance where it has been shown that activation of the hydroxysiliconate results in the formation of siloxide ion. We have also been able to generate the hydroxide adduct of phenyltrichlorosilane, and find that it loses only HCl upon CID. The hydroxide adduct of phenyltrimethyl-

silane was not observed upon reaction of the silane with solvated hydroxide.

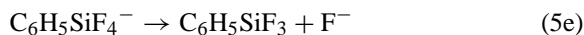
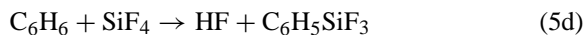
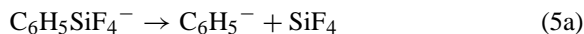
## 4. Discussion—ion affinities

In this section, we describe the determination of the fluoride and hydride affinities of phenyltrifluorosilane. We also report measured bond energies and barriers obtained upon CID of the other ions prepared.

### 4.1. Fluoride

The fluoride affinity of phenyltrifluorosilane could be determined directly if fluoride were formed upon CID of the  $\text{C}_6\text{H}_5\text{SiF}_4^-$  ion [45]. However, CID of  $\text{C}_6\text{H}_5\text{SiF}_4^-$  ion gives only phenide and  $\text{SiF}_4$ .

$$\begin{aligned} DH_{298}(\text{C}_6\text{H}_5\text{SiF}_3\text{--F}^-) &= \Delta H_{f,298}(\text{C}_6\text{H}_5\text{SiF}_3) + \Delta H_{f,298}(\text{HF}) \\ &\quad - \Delta H_{f,298}(\text{C}_6\text{H}_6) - \Delta H_{f,298}(\text{SiF}_4) \\ &\quad + \Delta H_{\text{acid},298}(\text{HF}) - \Delta H_{\text{acid},298}(\text{C}_6\text{H}_6) \\ &\quad + DH_{298}(\text{C}_6\text{H}_5^-\text{--SiF}_4) \end{aligned} \quad (5)$$



The fluoride affinity can be calculated from the  $\text{C}_6\text{H}_5^-\text{--SiF}_4$  bond dissociation enthalpy ( $DH_{298}(\text{C}_6\text{H}_5^-\text{--SiF}_4)$ ) according to Eq. (5), derived from the components in Eqs. (5a)–(5e). The  $\text{C}_6\text{H}_5^-\text{--SiF}_4$  bond dissociation enthalpy (Eq. (5a)) was obtained from energy-resolved CID of the  $\text{C}_6\text{H}_5\text{SiF}_4^-$  ion. The cross sections for formation of phenide as a function of energy are shown in Fig. 1. The solid line is the fully convoluted fit to the data, obtained using the procedures described in Section 2.

From the fit, the  $\text{C}_6\text{H}_5^-\text{--SiF}_4$  bond dissociation enthalpy is found to be  $2.86 \pm 0.11$  eV, with  $n = 1.5 \pm 0.1$ .

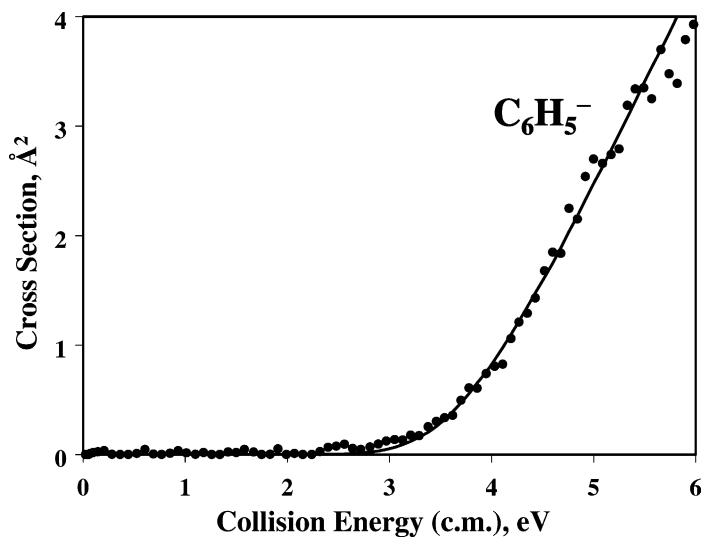


Fig. 1. Cross sections for phenide formation upon CID of  $C_6H_5SiF_4^-$  ion as a function of collision energy. The solid line is the fully convoluted fit to the data, as discussed in the text.

Table 1  
Supplemental thermochemical data (kcal/mol)

Species	Value	Reference
Heats of formation		
HF	$-65.32 \pm 0.17$	[15]
$C_6H_6$ (benzene)	$19.82 \pm 0.12$	[15]
$CH_3SiF_3$	$-294.6$	[60,61]
$C_6H_5CH_3$	$11.95 \pm 0.15$	[15]
$C_6H_5SiF_3$	$-257.5 \pm 2.0$	This work <sup>a</sup>
$CH_3CH_3$	$-20.04 \pm 0.07$	[15]
$SiF_4$	$-386.18 \pm 0.11$	[62]
$SiHF_3$	$-287.7 \pm 1.0$	[60,63]
$C_6H_5SiHF_2$	$-155.1 \pm 3.6$	This work <sup>b</sup>
$SiH_3F$	$-85.6 \pm 1.0$	[60,63]
$CH_3OH$	$-48.07 \pm 0.05$	[15]
$CH_3OSiF_3$	$-361.2 \pm 4.2$	This work <sup>c</sup>
$Si(OCH_3)_4$	$-282.0 \pm 1.2$	[44,64]
Gas-phase acidities		
HF	$371.6 \pm 0.2$	[52]
$C_6H_6$	$401.7 \pm 0.5$	[52]
$H_2$	$400.4$	[52]
$CH_3OH$	$381.6 \pm 0.7$	[65]

<sup>a</sup> Calculated at the G3(MP2) level of theory, using the isodesmic reaction in Eq. (6).

<sup>b</sup> Calculated at the G3(MP2) level of theory, using the isodesmic reaction in Eq. (9).

<sup>c</sup> Calculated at the G3(MP2) level of theory, using the isodesmic reaction in Eq. (10).

The heat of formation of  $SiF_4$ , and the heats of formation and gas-phase acidities of HF and  $C_6H_6$  required for the determination of the fluoride affinity are taken from Table 1. The only previously reported heat of formation of phenyltrifluorosilane was an estimate of  $-261$  kcal/mol [46], and so for this work we buttress the estimated value with a calculation. At the G3(MP2) level of theory [47,48], the 298 K enthalpy change for the isodesmic reaction in Eq. (6) is calculated to be  $-5.1$  kcal/mol (Table 2). The G3(MP2) computational approach is relatively new, but has been shown to work well for silanes and halogenated silane systems [49–51].



Table 2  
G3(MP2) energies used to determine  $\Delta H_{f,298}$  values of  $C_6H_5SiF_3$ ,  $C_6H_5SiF_2H$  and  $CH_3OSiF_3$ <sup>a</sup>

Species	$H_{298}$	Species	$H_{298}$
$C_6H_5SiF_3$	$-819.814493$	$SiF_4$	$-688.394598$
$C_6H_5CH_3$	$-271.061622$	$SiH_3F$	$-390.659094$
$CH_3SiF_3$	$-628.407712$	$CH_3OSiF_3$	$-703.577784$
$CH_3CH_3$	$-79.646714$	$Si(OCH_3)_4$	$-749.120826$
$C_6H_5SiHF_2$	$-720.565798$		

<sup>a</sup> 298 K enthalpy ( $H$ ) values, in Hartrees.

Table 3

Bond dissociation energies, reaction barriers, and thermochemical parameters measured in this work<sup>a</sup>

Directly measured energies		Derived thermochemical properties	
Bond dissociation enthalpies <sup>b</sup>		Fluoride affinity	
$C_6H_5SiF_4^- \rightarrow C_6H_5 + SiF_4$	$66.0 \pm 2.5$	$C_6H_5SiF_3$	$79.4 \pm 3.3$
$C_6H_5SiHF_3^- \rightarrow C_6H_5^- + SiHF_3$	$54.9 \pm 2.3$	$C_6H_5SiHF_2$	$72.3 \pm 4.4$
$C_6H_5SiF_3OCH_3^- \rightarrow C_6H_5^- + CH_3OSiF_3$	$60.9 \pm 3.5$		
$C_6H_5SiF_2O^- \rightarrow SiF_2O^- + C_6H_5$	$117.6 \pm 1.6$	Hydride affinity	
		$C_6H_5SiF_3$	$64.0 \pm 3.2$
Reaction barriers <sup>c</sup>		Methoxide affinity	
$C_6H_5SiHF_3^- \rightarrow SiF_3^- + C_6H_6$	$47.7 \pm 1.6$	$C_6H_5SiF_3$	$76.6 \pm 5.9$
$C_6H_5SiF_3OCH_3^- \rightarrow SiF_3O^- + C_6H_5CH_3$	$57.2 \pm 6.5$		
$C_6H_5SiF_2O^- \rightarrow C_6H_5O^- + SiF_2$	$85.8 \pm 4.6$		
$C_6H_5SiF_2O^- \rightarrow C_6H_4SiFO^- + HF$	$83.9 \pm 6.7$		

<sup>a</sup> Values in kcal/mol.<sup>b</sup> Values correspond to  $\Delta H_{298}$  values.<sup>c</sup> Energy barriers for the listed reactions, corresponding to  $\Delta E$  at 0 K, obtained from fits of energy-resolved CID cross sections. See text for transition state properties.

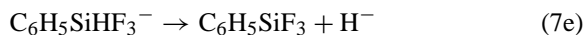
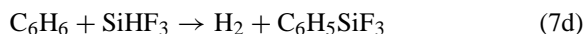
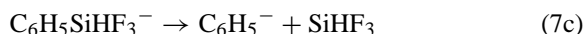
By using the heats of formation for the reference compounds (Table 1) we obtain  $\Delta H_{f,298}(C_6H_5SiF_3) = -257.5 \pm 2.0$  kcal/mol, which compares favorably to the previous estimate. From this value, we have determined a fluoride affinity (Eq. (5)) of  $79.4 \pm 3.3$  kcal/mol. The fluoride affinity of phenyltrifluorosilane is significantly higher than those of other silanes that have been examined, including methylfluorosilanes (38–51 kcal/mol) and tetrafluorosilane (62 kcal/mol) [16], and is similar to those for strong Lewis acids such as  $BF_3$  (81 kcal/mol) [52]. This suggests that the presence of the phenyl moiety on the silane leads to a greater stabilization of the tetrafluorosilicate anion. Measured bond dissociation energies and derived thermochemical properties are summarized in Table 3.

#### 4.2. Hydride

Attempts to generate the hydride adduct of phenyltrifluorosilane by direct addition of hydride ion or by hydride transfer from other hydride donors (such as  $n-BuSiH_4^-$ ) [9] were unsuccessful. However, the  $C_6H_5SiF_3H^-$  ion could be prepared in high yield by the reaction of phenyldifluorosilane,  $C_6H_5SiF_2H$ , with fluoride ion. CID of the  $C_6H_5SiF_3H^-$  ion proceeds by direct cleavage to give phenide ion,  $C_6H_5^-$ , and by

rearrangement to form the trifluorosilyl anion,  $SiF_3^-$ , and presumably benzene. The cross sections for formation of the products are shown as solid circles and triangles, respectively, in Fig. 2. In this case, we can use the  $C_6H_5^-SiHF_3$  bond dissociation energy to calculate the hydride affinity of  $C_6H_5SiF_3$ , as shown in Eq. (7), derived from Eqs. (7a)–(7e).

$$\begin{aligned}
 DH_{298}(C_6H_5SiF_3-H^-) &= \Delta H_{acid,298}(H_2) + \Delta H_{f,298}(C_6H_5SiF_3) \\
 &\quad - \Delta H_{acid,298}(C_6H_6) - \Delta H_{f,298}(C_6H_6) \\
 &\quad - \Delta H_{f,298}(SiHF_3) + DH_{298}(C_6H_5^-SiHF_3) \quad (7)
 \end{aligned}$$



The determination of the phenide-trifluorosilane BDE is complicated by the fact that two products are formed during CID, such that the energy threshold for the ion dissociation is subject to a kinetic shift. Therefore, the data are fit by including the branching ratios for the formation of the two products [32], where the branching ratios are calculated using RRKM theory.

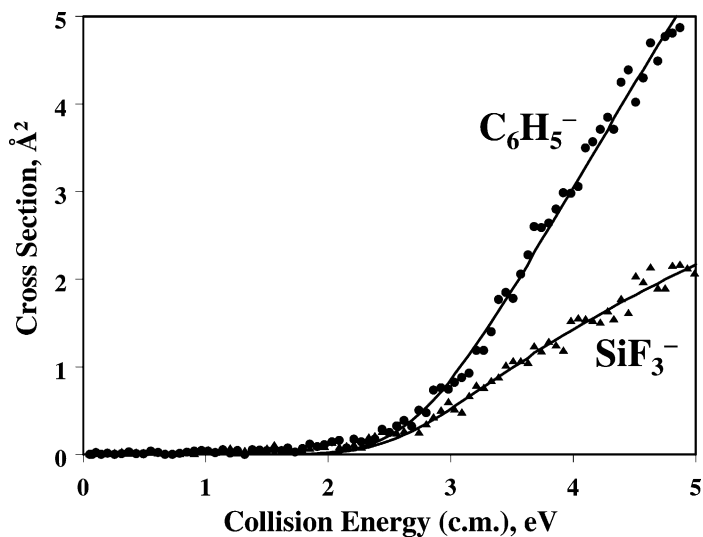


Fig. 2. Cross sections for CID of  $C_6H_5SiHF_3^-$  ion as a function of collision energy. The circles are cross sections for formation of phenyl anion whereas triangles are those for formation of  $SiF_3^-$  ion. The solid lines are the fully convoluted fits for the data, as discussed in the text.

For the modeling, the transition state for the formation of phenyl anion is assumed to be a loose, product-like structure in the phase-space limit. The properties of the transition state for formation of  $SiF_3^-$  are not known or easily computed, but can be determined empirically. The data were first fit by assuming a transition state similar to that of the reactant ion but with one reaction coordinate removed. The frequency removed was  $430.7\text{ cm}^{-1}$ , which corresponds to vibrational motion involving the stretching of the C–Si bond coupled with bending of the H–Si–C angle, suggesting formation of benzene and loss of  $SiF_3^-$ . The fit was then improved by adjusting the low-energy frequencies and tightening the transition state so as to reproduce the branching ratios for the products over the fitting range, which is chosen to include the steeply rising portions of the cross sections for all channels. However, the cross sections at energies far above the threshold cannot always be fit with this approach, because the dissociation is not necessarily statistical in that region [53]. The best fit to the data, shown as the solid lines in Fig. 2, was obtained with an activation entropy,  $\Delta S^\ddagger$ , of  $10.6\text{ cal/mol K}$  for  $SiF_3^-$  formation, and  $16.2\text{ cal/mol K}$  for the formation of phenide, and

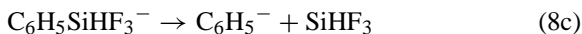
with  $n = 1.4 \pm 0.1$ . Although the empirically determined activation entropy likely reflects the partition function for the transition state, the actual frequencies for the transition state most likely do not agree with those used here. The activation entropy indicates that the formation of  $SiF_3^-$  proceeds by a very loose transition state, consistent with a mechanism that involves dissociation into phenyl anion and  $SiHF_3$ , followed by proton transfer. The measured bond dissociation energy for direct dissociation and the energy barrier for formation of  $SiF_3^-$  are included in Table 3.

From the modeling of the data, the dissociation enthalpy for formation of phenyl anion and  $SiHF_3$  is found to be  $54.9 \pm 2.3\text{ kcal/mol}$ . By using the measured dissociation enthalpy and the supplemental thermochemical data listed in Table 1 with Eq. (7), the hydride affinity of  $C_6H_5SiF_3$  is calculated to be  $64.0 \pm 3.2\text{ kcal/mol}$ . Therefore, the hydride affinity of  $C_6H_5SiF_3$  is significantly higher than those for alkyl silanes, which are generally about  $20\text{ kcal/mol}$  [9], and is comparable to the hydride affinities of strong Lewis acids, such as  $BH_3$  ( $DH_{298}(BH_3-H^-) = 74.2 \pm 2.8\text{ kcal/mol}$ ) [54]. The comparison between the hydride affinities of  $C_6H_5SiF_3$  and  $BH_3$  is in-

triguing, as it suggests that the  $C_6H_5SiF_3H^-$  ion is comparable in stability to the borohydride ion,  $BH_4^-$ , a common reducing agent used in chemical synthesis. In fact, fluorophenylsiliconate ions, generated in situ by reaction of either phenylsilane or diphenylsilane with CsF, have previously been employed as hydride donors to reduce esters, aldehydes, and ketones [55–58]. The hydride affinity is given in Table 3.

The fluoride affinity of phenyldifluorosilane can also be calculated from the measured dissociation enthalpy of  $C_6H_5SiHF_3^-$  according to Eq. (8) (derived from Eqs. (8a)–(8e)). As above, the heats of formation and gas-phase acidities (Table 1) were taken from the literature, except for the heat of

$$\begin{aligned} DH_{298}(C_6H_5SiHF_2-F^-) &= \Delta H_{f,298}(C_6H_5SiHF_2) + \Delta H_{f,298}(HF) \\ &+ \Delta H_{acid,298}(HF) - \Delta H_{acid,298}(C_6H_6) \\ &- \Delta H_{f,298}(C_6H_6) - \Delta H_{f,298}(SiHF_3) \\ &+ DH_{298}(C_6H_5^- - SiHF_3) \end{aligned} \quad (8)$$



formation of phenyldifluorosilane, which was estimated computationally from G3(MP2) calculations using theisodesmic reaction shown in Eq. (9). The quantity  $\Delta H_{f,298}(C_6H_5SiHF_2)$  was determined to be  $-155.1 \pm 3.6$  kcal/mol.



The derived fluoride affinity of phenyldifluorosilane is  $72.3 \pm 4.4$  kcal/mol, only 7 kcal/mol less than that for phenyltrifluorosilane, indicating that the fluoride adduct of phenyldifluorosilane is almost as stable as the tetrafluorosiliconate ion. Therefore, the results obtained here suggest that phenyldifluorosilane could be converted into an isolable crystalline reducing agent,  $C_6H_5SiF_3H^-$ , upon reaction with  $F^-$  in solution. The

fluoride affinity of phenyldifluorosilane is also listed in Table 3.

#### 4.3. Methoxide

Methoxide reacts with phenyltrifluorosilane to produce a pentavalent adduct,  $C_6H_5SiF_3OCH_3^-$ . This adduct undergoes CID via two pathways. A direct dissociation pathway leads to the formation of phenide and  $CH_3OSiF_3$ , and rearrangement yields  $SiF_3O^-$ , and presumably toluene. Cross sections are shown in Fig. 3. At 25 eV (lab), the cross section for formation of phenide is  $8 (\pm 4) \text{ \AA}^2$ , and the relative cross section for the  $SiF_3O^-$  formation is approximately 1/10 of that for phenide formation. Because two ionic products are formed, the appearance energy for phenide is subject to a competitive shift. Modeling of the data requires the incorporation of the branching ratios for the two products, as described above for the  $C_6H_5SiHF_3^-$  ion. As before, the transition state for the direct dissociation process (formation of  $C_6H_5^-$ ) is assumed to be a loose, product-like structure in the phase-space limit. The properties of the transition state for the rearrangement process are determined empirically to reproduce the branching ratio of the products over the steeply rising portions of the appearance curves. The optimal activation entropies for formation of phenide and  $SiF_3O^-$  are 21.4 and 15.4 cal/mol K, respectively. The activation entropy for formation of phenide indicates a loose transition state, as assumed for the direct cleavage reaction. Alternatively, the activation entropy for formation of  $SiF_3O^-$  also indicates a rather loose transition state, which is surprising

for a rearrangement process. A possible mechanism for dissociation of the ion that is consistent with the high activation entropy is a stepwise process, wherein the first step is direct dissociation to form the methoxytrifluorosilane, with subsequent transfer of a methyl cation to phenide. Fitting replicate data sets gives a phenide–methoxytrifluorosilane bond dissociation enthalpy of  $2.64 \pm 0.15$  eV, an activation



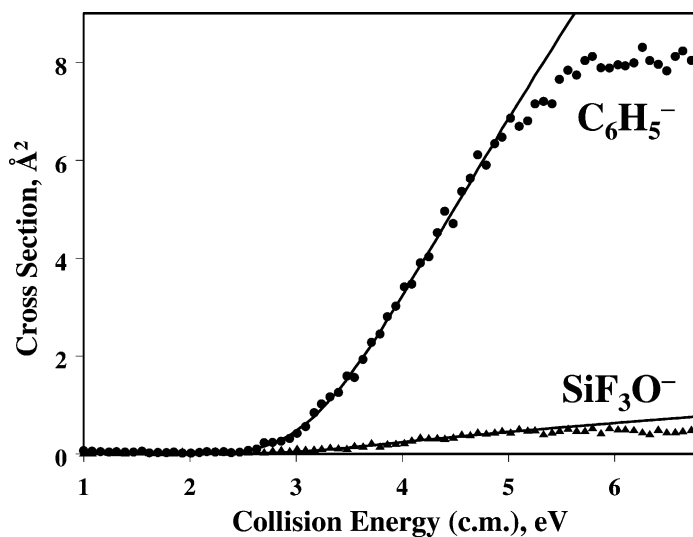


Fig. 3. Cross sections for CID of  $\text{C}_6\text{H}_5\text{SiF}_3\text{OCH}_3^-$  ion as a function of collision energy. The circles are cross sections for formation of phenyl anion whereas triangles are those for formation of  $\text{SiF}_3\text{O}^-$  ion. The solid lines are the fully convoluted fits for the data, as discussed in the text.

barrier for formation of  $\text{SiF}_3\text{O}^-$  of  $2.48 \pm 0.28$  eV, and  $n = 1.3 \pm 0.2$ .

Determination of the methoxide affinity of phenyltrifluorosilane requires the enthalpy of formation of  $\text{CH}_3\text{OSiF}_3$ , which was calculated from G3(MP2) calculations for the isodesmic reaction given in Eq. (10). The heat of formation for  $\text{CH}_3\text{OSiF}_3$  was determined to be  $-361.2 \pm 4.2$  kcal/mol with this method.



The methoxide affinity of phenyltrifluorosilane can be determined from the bond dissociation energy of the methoxide adduct of  $\text{C}_6\text{H}_5\text{SiF}_3$  to  $\text{C}_6\text{H}_5^-$  and  $\text{CH}_3\text{OSiF}_3$ , using procedures analogous to those above. The methoxide affinity is calculated using Eq. (11), derived from Eqs. (11a)–(11e).

$$\begin{aligned} DH_{298}(\text{C}_6\text{H}_5\text{SiF}_3\text{OCH}_3^-) &= \Delta H_{\text{acid},298}(\text{CH}_3\text{OH}) + \Delta H_{\text{f},298}(\text{CH}_3\text{OH}) \\ &+ \Delta H_{\text{f},298}(\text{C}_6\text{H}_5\text{SiF}_3) - \Delta H_{\text{acid},298}(\text{C}_6\text{H}_6) \\ &- \Delta H_{\text{f},298}(\text{C}_6\text{H}_6) - \Delta H_{\text{f}}(\text{CH}_3\text{OSiF}_3) \\ &+ DH_{298}(\text{C}_6\text{H}_5^- - \text{CH}_3\text{OSiF}_3) \end{aligned} \quad (11)$$



The methoxide affinity,  $DH_{298}(\text{C}_6\text{H}_5\text{SiF}_3\text{OCH}_3^-)$  was determined to be  $76.6 \pm 5.9$  kcal/mol. The uncertainty of this value is somewhat higher than the previous determinations in this work because this result relies upon two calculated heats of formation ( $\text{C}_6\text{H}_5\text{SiF}_3$  and  $\text{SiF}_3\text{OCH}_3$ ).

#### 4.4. Hydroxide

Hydroxide reacts with  $\text{C}_6\text{H}_5\text{SiF}_3$  to give difluorophenylsiloxide,  $\text{C}_6\text{H}_5\text{SiF}_2\text{O}^-$ . Upon CID,  $\text{C}_6\text{H}_5\text{SiF}_2\text{O}$  fragments to give  $\text{SiF}_2\text{O}^-$  by loss of phenyl radical. Phenoxide ion,  $\text{C}_6\text{H}_5\text{O}^-$  (loss of  $\text{SiF}_2$ ), and a  $\text{C}_6\text{H}_4\text{SiFO}^-$  ion with unidentified structure (loss of HF), are also observed. The CID cross sections are shown in Fig. 4. The data were modeled taking into account the branching ratios for the dissociation, as described for the ions above. For

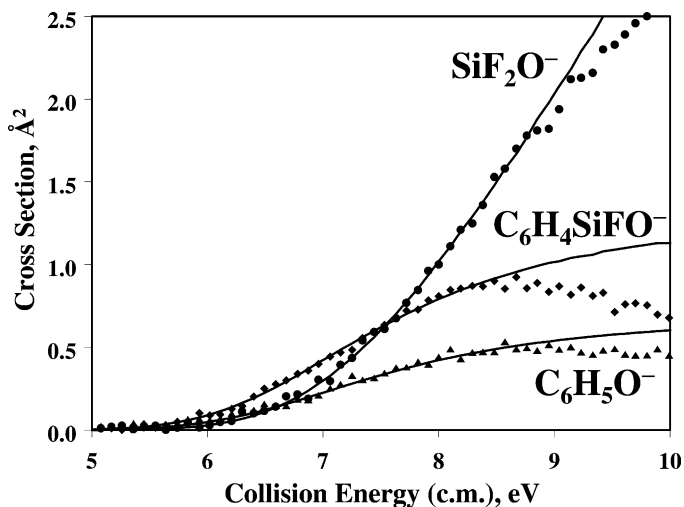


Fig. 4. Cross sections for CID of  $C_6H_5SiF_2O^-$  ion as a function of collision energy. The circles are cross sections for formation of  $SiF_2O^-$ . The triangles represent the rearrangement giving phenoxide, whereas diamonds represent rearrangement resulting in loss of HF. The solid lines are the fully convoluted fits for the data, as discussed in the text.

this system, the formation of  $SiF_2O^-$  was assumed to have a loose, product-like transition state, and while the activation entropies for the rearrangement channels were empirically obtained from a statistical least-square deviation approach. From the modeling, the bond energy for formation of  $SiF_2O^-$ ,  $DH_{298}(C_6H_5-SiF_2O^-)$ , is found to be  $5.10 \pm 0.07$  eV ( $117.6 \pm 1.6$  kcal/mol). The activation barriers for formation of  $C_6H_5O^-$  and  $C_6H_4SiFO^-$  are  $3.72 \pm 0.20$  and  $3.64 \pm 0.29$  eV, respectively. The value of  $n$  is  $1.0 \pm 0.2$ . Whereas the transition state for loss of phenyl radical is assumed to be loose, with  $\Delta S^\ddagger = 19.2$  cal/mol K, the activation entropies for the formation of  $C_6H_5O^-$  and  $C_6H_4SiFO^-$  are  $-2.0$  and  $-1.7$  cal/mol K, respectively, consistent with values expected for rearrangement processes with tight transition states. The formation of  $SiF_2O^-$  as opposed to phenyl anion indicates that the electron affinity of difluorosilaformaldehyde,  $SiF_2O$ , is very high, higher than that of phenyl radical,  $1.096 \pm 0.006$  eV [59]. The hydroxide adduct ion undergoes two rearrangement pathways upon CID to lose HF forming  $C_6H_5SiF_2O^-$  as the major ionic product, and a minor pathway with loss of benzene forming  $SiF_3O^-$ . Modeling of these data will be described in future publications.

## 5. Conclusions

The results obtained in this work show phenyltrifluorosilane to be a strong Lewis acid, with ion affinities that are similar to those observed for boranes. Therefore, phenyltrifluorosilane is a potential organic reagent that can be used as a strong Lewis acid. Moreover, the strong affinity for hydride suggests that the phenyltrifluorohydrosilicate ion,  $C_6H_5SiF_3H^-$ , prepared by the reaction of phenyldifluorosilane with fluoride, is a potential stable hydride reducing agent. Investigations into this possibility are in progress.

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