

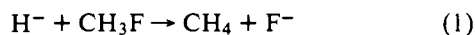
# Gas-Phase SN2 Reactions at Silicon and Carbon Centers. An Experimental Appraisal of Theory

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**Abstract:** The gas-phase kinetics of the reactions of H<sup>-</sup>, D<sup>-</sup>, OH<sup>-</sup>, ·C<sup>-</sup>, ·C<sub>2</sub><sup>-</sup>, ·C<sub>4</sub><sup>-</sup>, and C<sub>4</sub>H<sup>-</sup> with SiH<sub>4</sub> and the reactions of D<sup>-</sup>, OH<sup>-</sup>, ·C<sup>-</sup>, ·C<sub>2</sub><sup>-</sup>, and C<sub>2</sub>H<sup>-</sup> with CH<sub>4</sub> have been investigated at 297 ± 2 K using the flowing afterglow technique. The reactions with silane are characterized by a variety of channels and reaction efficiencies whereas methane was observed to be relatively unreactive. The rate constants measured for the reactions of H<sup>-</sup> and D<sup>-</sup> with SiH<sub>4</sub> and D with CH<sub>4</sub> are in accord with the energies of the reaction intermediates SiH<sub>5</sub><sup>-</sup> and CH<sub>5</sub><sup>-</sup> predicted by ab initio quantum mechanical calculations but do not corroborate the prediction of a reaction barrier for the attack of H<sup>-</sup> on silane. This latter reaction, for which the SN2 channel is observed to compete with proton transfer, proceeds rapidly at 297 K.

The intrinsic energy surfaces of bimolecular nucleophilic substitution (SN2) reactions, which have been studied extensively in a variety of solvents, have recently become the subject of a number of ab initio and semiempirical molecular orbital calculations.<sup>2-10</sup> Although calculations have been reported which also explore the influence of solvent on the intrinsic energetics of such reactions,<sup>11</sup> computational difficulties have generally prevented the incorporation of solvent effects into such calculations so that their direct comparison with measurements made in solution have been of limited value. Fortunately, gas-phase techniques have now become available which allow the direct experimental investigation of SN2 reactions proceeding in the absence of solvent molecules, viz., in vacuo.<sup>12-15</sup> It has, therefore, become possible to conduct measurements on several specific SN2 reactions which have been scrutinized through molecular orbital calculations, and, consequently, to compare directly theoretical predictions with experiment. So far the experimental measurements have been restricted to specific rates of reaction at room temperature. The extent of the comparisons with theory has therefore been limited but the comparisons have nevertheless proven to be valuable. For example, quantum mechanical studies by Dedieu and Veillard<sup>5</sup> and by Bader, Duke, and Messer<sup>6</sup> had predicted energy barriers of 3.8 and 22 kcal mol<sup>-1</sup>, respectively, for the SN2 reactions

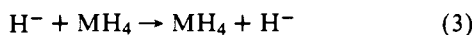


and



The rate constants for these reactions at 296 K were subsequently measured in a flowing afterglow.<sup>14</sup> When considered in the context of the traditional Arrhenius model, albeit somewhat over-simplified, the experimental values for the rate constants were consistent with activation energies of 3.6 and ≥5 kcal mol<sup>-1</sup>, respectively, in good agreement with the theoretical predictions. These results provided, for the first time, a direct experimental measure of confidence for these quantum mechanical studies.

In this paper we wish to report gas-phase measurements which provide an empirical test for recent theoretical studies of the athermal symmetric silyl and methyl cation transfer reactions



where M = Si and C. The energy surfaces of both reactions have been explored in a number of calculations. Recently Baybutt<sup>2</sup> has performed ab initio molecular orbital calculations

in a comparative study of these two systems. He concludes that the carbon system should show a barrier to reaction since the reaction complex is of much higher energy (ca. +60 kcal mol<sup>-1</sup>) than the reactants, unlike the silicon system for which the reaction complex is of lower energy (ca. -19 kcal mol<sup>-1</sup>). Wilhite and Spialter<sup>4</sup> have performed both semiempirical CNDO and ab initio calculations for a number of points along the H<sup>-</sup> + SiH<sub>4</sub> reaction coordinate (approach of the hydride ion to a face of the tetrahedron of silane). They found that, whereas the CNDO calculation did not indicate a barrier to reaction, further ab initio calculations along the CNDO path predicted a barrier of 8.6 kcal mol<sup>-1</sup>. The reaction complex SiH<sub>5</sub><sup>-</sup> (a trigonal-bipyramidal form) was again found to be stable (by 16.9 kcal mol<sup>-1</sup>) with respect to silane and the hydride ion.

The reactions of other nucleophiles (including several radical anions) with SiH<sub>4</sub> and CH<sub>4</sub> have also been explored in the present study, in part to provide further experimental observations with which future calculations can perhaps be compared.

## Experimental Section

The experiments were performed using a flowing afterglow apparatus which has been described previously in detail.<sup>16</sup> Briefly, helium or hydrogen is flowed down a 1.4 m, 8.9 cm diameter stainless steel tube at a velocity of ~10<sup>4</sup> cm s<sup>-1</sup> and at a pressure of ~0.3 Torr. A plasma containing the reactant ion of interest is generated at one end of the tube by electron impact on an appropriate neutral gas and sampled at the other end by a small on-axis leak coupled to a quadrupole mass spectrometer. The decline of the initial ion signal as seen by the mass spectrometer as a function of neutral reactant addition upstream of the sampling orifice affords a measure of the rate constant. The method of data analysis has also been discussed previously in considerable detail.<sup>16</sup>

In the present experiments CH<sub>4</sub>(CD<sub>4</sub>) and C<sub>2</sub>H<sub>2</sub> were bombarded with energetic electrons (40-60 eV) to produce the anions of interest. Under typical operating conditions the addition of CH<sub>4</sub> produced (in order of decreasing abundance) C<sub>2</sub>H<sup>-</sup>, ·C<sub>2</sub><sup>-</sup>, ·C<sup>-</sup>, and H<sup>-</sup> while the addition of CD<sub>4</sub> resulted in the corresponding deuterated species. The addition of C<sub>2</sub>H<sub>2</sub> produced (in order of decreasing abundance) C<sub>2</sub>H<sup>-</sup>, ·C<sub>2</sub><sup>-</sup>, C<sub>4</sub>H<sup>-</sup>, ·C<sub>4</sub><sup>-</sup>, and ·C<sup>-</sup>.

The ions produced in the electron-impact region spend several milliseconds in the flowing plasma and undergo several thousand collisions with the buffer gas before they enter the reaction region. Consequently we believe that the anionic species involved in reaction have internal and translational energy distributions which are Maxwell-Boltzmann and are characterized by the temperature of the flowing plasma which is determined by the temperature of the wall of the stainless steel flow tube. The neutral reagent is added already in thermal equilibrium with the wall. The wall temperature is taken to be equal to the room temperature of 297 ± 2 K.

Table I. Rate Constants and Product Channels for Reactions of Anions with SiH<sub>4</sub> at 297 ± 2 K

Reaction	$k_{\text{exptl}}^a$	$k_c^b$
H <sup>-</sup> + SiH <sub>4</sub> → SiH <sub>3</sub> <sup>-</sup> + H <sub>2</sub>	0.57 ± 0.05 (3)	4.95
D <sup>-</sup> + SiH <sub>4</sub> → SiH <sub>3</sub> D <sup>-</sup> + H <sup>-</sup>	2.2 ± 0.5 (4)	3.56
→ SiH <sub>2</sub> D <sup>-</sup> + H <sub>2</sub>		
→ SiH <sub>3</sub> <sup>-</sup> + HD		
OH <sup>-</sup> + SiH <sub>4</sub> → SiH <sub>3</sub> O <sup>-</sup> + H <sub>2</sub> O	1.3 ± 0.2 (3)	1.46
→ SiH <sub>3</sub> O <sup>-</sup> + H <sub>2</sub>		
·C <sup>-</sup> + SiH <sub>4</sub> → SiH <sub>3</sub> <sup>-</sup> + ·CH	0.062 ± 0.005 (5)	1.65
·C <sub>2</sub> <sup>-</sup> + SiH <sub>4</sub> → C <sub>2</sub> SiH <sub>3</sub> <sup>-</sup> + ·H	0.37 ± 0.02 (4)	1.32
→ (SiH <sub>3</sub> <sup>-</sup> + ·C <sub>2</sub> H)		
·C <sub>4</sub> <sup>-</sup> + SiH <sub>4</sub> → C <sub>4</sub> SiH <sub>3</sub> <sup>-</sup> + ·H	0.084 ± 0.010 (3)	1.11
→ (SiH <sub>3</sub> <sup>-</sup> + ·C <sub>4</sub> H)		
C <sub>2</sub> H <sup>-</sup> + SiH <sub>4</sub> →	≤ 0.006	1.30
C <sub>4</sub> H <sup>-</sup> + SiH <sub>4</sub> →	≤ 0.005	1.11
Cl <sup>-</sup> + SiH <sub>4</sub> →	≤ 0.002	1.19
NO <sub>2</sub> <sup>-</sup> + SiH <sub>4</sub> →	≤ 0.003	1.12

<sup>a</sup>The mean value of the experimentally determined rate constant in units of 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The limits given along with the mean value represent the precision of the measurements. The number of measurements is given in parentheses. <sup>b</sup>The calculated collision rate constant in units of 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> according to the Langevin theory, ref 17, with α(SiH<sub>4</sub>) = 4.34 Å<sup>3</sup>, ref 18.

Table II. Rate Constants for Reactions of Anions with CH<sub>4</sub> at 297 ± 2 K

Reaction	$k_{\text{exptl}}^a$	$k_c^b$
H <sup>-</sup> + CD <sub>4</sub> → CD <sub>3</sub> H + D <sup>-</sup>	≤ 0.001	3.8
D <sup>-</sup> + CH <sub>4</sub> → CH <sub>3</sub> D + H <sup>-</sup>	≤ 0.0001	2.83
OH <sup>-</sup> + CH <sub>4</sub> →	≤ 0.001 <sup>c</sup>	1.32
·C <sup>-</sup> + CH <sub>4</sub> →	≤ 0.0001 <sup>d</sup>	1.44
·C <sub>2</sub> <sup>-</sup> + CH <sub>4</sub> →	≤ 0.0001 <sup>d</sup>	1.22
C <sub>2</sub> H <sup>-</sup> + CH <sub>4</sub> →	≤ 0.0001 <sup>d</sup>	1.21

<sup>a</sup>Experimentally determined upper limits to the rate constants in units of 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup>The calculated collision rate constant in units of 10<sup>-9</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> according to the Langevin theory, ref 17, with α(CH<sub>4</sub>) = 2.56 Å<sup>3</sup>, ref 19. α(CD<sub>4</sub>) is taken to be equal to α(CH<sub>4</sub>). <sup>c</sup>Previous flowing afterglow results, ref 20. <sup>d</sup>Previous flowing afterglow results, ref 21.

The following gases were used: helium (Linde, Prepurified Grade, 99.995% He), hydrogen (Linde, 99.95% H<sub>2</sub>), methane (Matheson Ultra High Purity, 99.97% CH<sub>4</sub>), acetylene (Matheson, Purified Grade, 99.6% C<sub>2</sub>H<sub>2</sub>), CD<sub>4</sub> (Merck Sharp and Dohme, 99 atom % D), and SiH<sub>4</sub> (Matheson, Semiconductor Grade, 99.95% SiH<sub>4</sub>).

## Results

The rate constant measurements are summarized in Tables I and II. The best estimate of a true value is taken to be the mean of a series of measurements. The limits given along with the mean value throughout this section represent the best estimate of the precision.<sup>22</sup> Sources of error have been described previously.<sup>16</sup> The absolute accuracy of the reported rate constants is estimated to be ±20%.

**H<sup>-</sup> + SiH<sub>4</sub>.** H<sup>-</sup> was observed to react with SiH<sub>4</sub> upon the addition of the latter into a flowing CH<sub>4</sub>-He plasma in which H<sup>-</sup> was initially a dominant negative ion. Figure 1 is representative of the observations made in three experiments in which the effective reaction length, *L*, was fixed at 60 cm, the gas velocity, *v*, had values from 8.3 to 8.5 × 10<sup>3</sup> cm s<sup>-1</sup>, and the total gas pressure was in the range 0.385–0.424 Torr. The OH<sup>-</sup> initially present in the reaction region can be attributed to trace amounts of H<sub>2</sub>O impurities in the flowing plasma. The disappearance of H<sup>-</sup> was accompanied by the production of SiH<sub>3</sub><sup>-</sup> which is indicative of the occurrence of the proton-transfer reaction

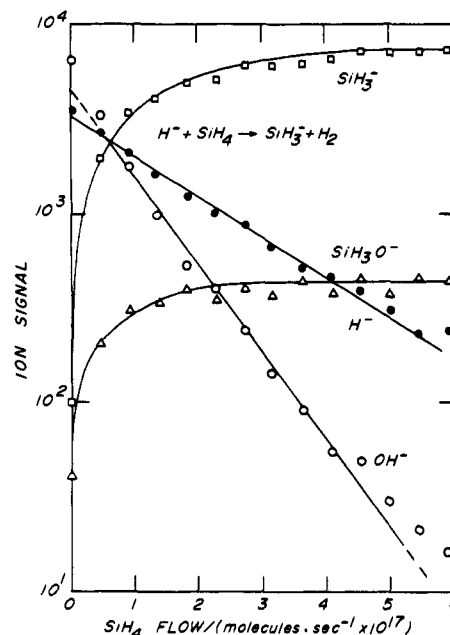
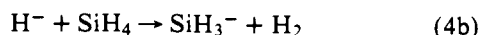
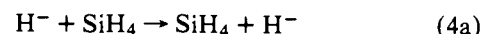


Figure 1. The variation of negative ion signals recorded upon the addition of SiH<sub>4</sub> into a flowing CH<sub>4</sub>-He plasma: *T* = 296 K, *P* = 0.424 Torr, CH<sub>4</sub> flow = 9.5 × 10<sup>17</sup> molecules s<sup>-1</sup>, *L* = 60 cm, and *v* = 8.3 × 10<sup>3</sup> cm s<sup>-1</sup>.

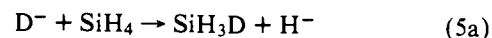
The production of SiH<sub>3</sub>O<sup>-</sup> must be attributed to the reaction of OH<sup>-</sup> with SiH<sub>4</sub> which was investigated independently in separate experiments which will be described later in this section. The three measurements of the H<sup>-</sup> decay provided a value for  $k_{4b} = (5.7 \pm 0.5) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The identification of the displacement channel



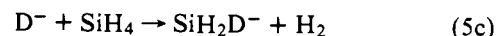
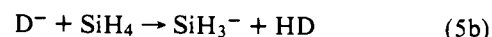
was precluded in these experiments since the mass spectrometer could not distinguish between reactant and product H<sup>-</sup> ions. Attempts were therefore made to observe this channel using the isotopic species, D<sup>-</sup>, as the nucleophile.

**D<sup>-</sup> + SiH<sub>4</sub>.** D<sup>-</sup> was generated from CD<sub>4</sub> introduced into the helium buffer gas upstream from the electron gun and, as shown in Figure 2, was observed to react rapidly with SiH<sub>4</sub> added downstream. Figure 2 includes the increase of the stoichiometrically allowed product ion signals which were observed to accompany the D<sup>-</sup> signal decay and also shows the presence and reaction of other major negative ions, viz., OH<sup>-</sup> and C<sub>2</sub>D<sup>-</sup>. Not shown are the ions OD<sup>-</sup>, ·C<sub>2</sub><sup>-</sup>, and ·C<sup>-</sup> which were also observed to be present and to react with SiH<sub>4</sub>.

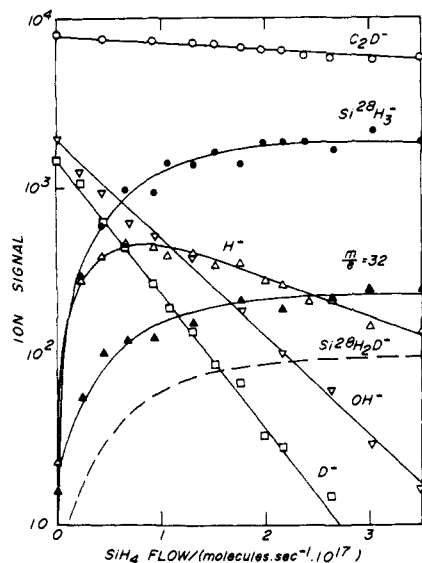
The production of H<sup>-</sup> can be ascribed solely to the reaction of D<sup>-</sup> with SiH<sub>4</sub> since separate experiments conducted in the absence of D<sup>-</sup> and to be described in the next two sections indicated that the hydride ion is not a product of the reaction of OH<sup>-</sup>, ·C<sup>-</sup>, ·C<sub>2</sub><sup>-</sup>, or C<sub>2</sub>H<sup>-</sup> with SiH<sub>4</sub>. Furthermore, the magnitude of the increase in the H<sup>-</sup> signal indicates that H<sup>-</sup> displacement is the main channel of the reaction of D<sup>-</sup> with SiH<sub>4</sub>:



We estimate that this channel is preferred by at least 4 to 1 over the channels:



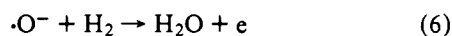
The reactions of the other aforementioned negative ions present in the flowing plasma as well as mass discrimination in the mass spectrometer sampling and detection system



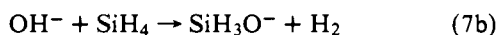
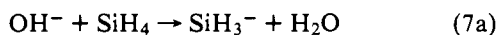
**Figure 2.** The variation of negative ion signals recorded upon addition of  $\text{SiH}_4$  into a flowing  $\text{CD}_4$ -He plasma. Not shown are the ions  $\text{OD}^-$ ,  $\text{C}_2^-$ , and  $\text{C}^-$  which were also observed to react with  $\text{SiH}_4$ . The slope of the  $\text{D}^-$  decay provides a rate constant of  $2.21 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ;  $T = 295 \text{ K}$ ,  $P = 0.298 \text{ Torr}$ ,  $\text{CD}_4$  flow =  $3.06 \times 10^{18} \text{ molecules s}^{-1}$ ,  $L = 60 \text{ cm}$ , and  $\bar{v} = 8.4 \times 10^3 \text{ cm s}^{-1}$ . The production of  $^{28}\text{SiH}_2\text{D}^-$  (dashed curve) is determined from the production of  $m/e 32$  by subtracting the contribution to  $m/e 32$  by the isotopic ion  $^{29}\text{SiH}_3^-$ .

prevented an unequivocal assignment of the actual branching ratio of channels 5a, 5b, and 5c. Four measurements of the  $\text{D}^-$  decay provided a value for  $k_5 = (2.2 \pm 0.5) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $L = 60 \text{ cm}$ ,  $\bar{v} = 7.9$  to  $8.4 \times 10^3 \text{ cm s}^{-1}$ , and  $P = 0.268$ - $0.353 \text{ Torr}$ .

**$\text{OH}^- + \text{SiH}_4$ .** In order to determine the specific rate and product channels for the reaction of  $\text{OH}^-$  with  $\text{SiH}_4$ , the latter was added into a  $\text{H}_2\text{O}$ -He plasma in which  $\text{OH}^-$  and  $\text{O}^-$  were initially dominant negative ions. Both  $\text{OH}^-$  and  $\text{O}^-$  were observed to react rapidly with  $\text{SiH}_4$  to produce  $\text{SiH}_3^-$  and  $\text{SiH}_3\text{O}^-$ . In order to elucidate the branching ratio of the  $\text{OH}^-$  reaction the experiment was repeated in a hydrogen buffer in which complications due to the  $\cdot\text{O}^-$  reaction could be avoided since  $\cdot\text{O}^-$  reacts rapidly with  $\text{H}_2$  by associative detachment, viz.



The results of an experiment conducted with a hydrogen buffer are shown in Figure 3. The two product channels observed were:

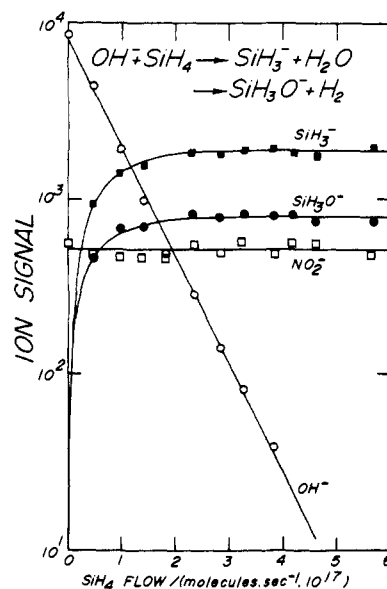


Proton transfer is the preferred channel by about 2:1. The displacement reaction:



would be difficult to observe under these operating conditions since  $\text{H}^-$  reacts rapidly with  $\text{H}_2\text{O}$  to produce  $\text{OH}^-$ . However, in a separate experiment (in pure He) in which  $\text{OH}^-$  was present as an impurity ion and  $\text{H}_2\text{O}$  was essentially absent, the addition of  $\text{SiH}_4$  did not give rise to  $\text{H}^-$ . We, therefore, conclude that channel 7c can only be a minor channel in the reaction of  $\text{OH}^-$  with  $\text{SiH}_4$ .

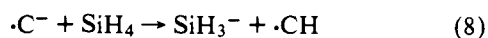
Three experiments (two in He at 0.319 and 0.504 Torr and one in  $\text{H}_2$  at 0.277 Torr) yielded a value for  $k_7$  of  $(1.3 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The reaction length was fixed at 60 cm and  $\bar{v}$  had values in the range 7.7 to  $8.6 \times 10^3 \text{ cm s}^{-1}$ .



**Figure 3.** Variation of negative ion signals recorded upon addition of  $\text{SiH}_4$  into a flowing  $\text{H}_2\text{O}$ - $\text{H}_2$  plasma. The slope of the  $\text{OH}^-$  decay yields a rate constant of  $1.38 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .  $\text{SiH}_3^-$  and  $\text{SiH}_3\text{O}^-$  were the only product ions observed:  $T = 297 \text{ K}$ ,  $P = 0.277 \text{ Torr}$ ,  $\text{H}_2\text{O}$  flow  $\sim 10^{17} \text{ molecules s}^{-1}$ ,  $L = 60 \text{ cm}$ , and  $\bar{v} = 7.7 \times 10^3 \text{ cm s}^{-1}$ .

**$\text{C}_x\text{H}_y^- + \text{SiH}_4$ .** The reactions of carbonaceous anions with  $\text{SiH}_4$  were explored further by adding  $\text{SiH}_4$  into a flowing  $\text{C}_2\text{H}_2$ -He plasma. Figure 4 shows the observed variations of negative ion signals. The slope of the decay of each anion provides a measure of the rate constant for the reaction of that anion with  $\text{SiH}_4$ . Five experiments were performed in which one or more of the anions  $\cdot\text{C}^-$ ,  $\cdot\text{C}_2^-$ ,  $\text{C}_2\text{H}^-$ ,  $\cdot\text{C}_4^-$ , and  $\text{C}_4\text{H}^-$  were monitored as a function of  $\text{SiH}_4$  addition. The rate constants determined for their reactions with  $\text{SiH}_4$  are included in Table I. The impurity ions  $\text{Cl}^-$  and  $\text{NO}_2^-$  were observed not to react. In these five experiments the  $\text{C}_2\text{H}_2$  flow had values in the range  $5.97 \times 10^{17}$  to  $2.32 \times 10^{18} \text{ molecules s}^{-1}$ .  $P$  was in the range 0.304-0.370 Torr,  $\bar{v}$  in the range 7.9 to  $8.3 \times 10^3 \text{ cm s}^{-1}$ , and the reaction length,  $L$ , had values of 59 and 85 cm.

The nature of the product ion spectrum and its variation with  $\text{SiH}_4$  addition suggest that  $\cdot\text{C}^-$  reacts with  $\text{SiH}_4$  mainly by proton transfer according to:

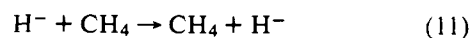


and that  $\cdot\text{C}_2^-$  and  $\cdot\text{C}_4^-$  react at least in part by H-atom displacement according to:

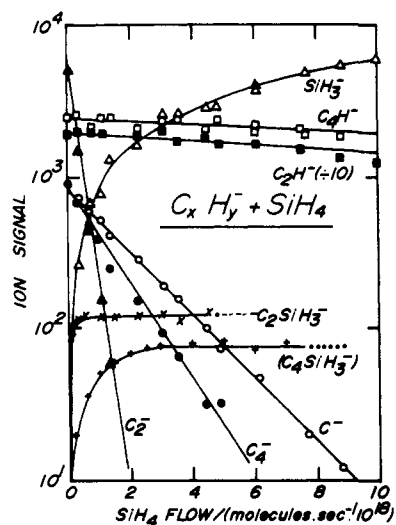


There was no evidence for the formation of  $\cdot\text{CSiH}_3$  through H-atom displacement by  $\cdot\text{C}^-$ . Also some of the  $\text{SiH}_3^-$  ions appear to be produced by slow proton transfer reactions of  $\text{C}_2\text{H}^-$  and/or  $\text{C}_4\text{H}^-$  with  $\text{SiH}_4$ . There was no evidence for the occurrence of H- displacement which, for the adopted experimental conditions, would be reflected by an initial increase in the  $\text{C}_2\text{H}^-$  signal since any  $\text{H}^-$  produced would react rapidly by proton transfer with the  $\text{C}_2\text{H}_2$  present in the flowing plasma. The observation of  $\text{H}^-$  was, however, rendered difficult by the large initial  $\text{C}_2\text{H}^-$  signal.

**$\text{D}^- + \text{CH}_4$ .** As was the case for reaction 4a, the identification of the displacement channel

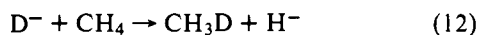


was prevented in these experiments by the inability of the



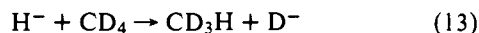
**Figure 4.** A comparison of the rates of reaction of various carbonaceous anions with  $\text{SiH}_4$  which is added to a flowing  $\text{C}_2\text{H}_2$ -He plasma. The slope of the  $\text{C}^-$  decay corresponds to a rate constant  $k = 5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ;  $T = 298 \text{ K}$ ,  $P = 0.304 \text{ Torr}$ ,  $\text{C}_2\text{H}_2$  flow =  $6.0 \times 10^{17} \text{ molecules s}^{-1}$ ,  $L = 60 \text{ cm}$ , and  $\bar{v} = 7.9 \times 10^3 \text{ cm s}^{-1}$ . The identification of  $\text{C}_4\text{SiH}_3^-$  was not unequivocal since this product ion could only be observed at low resolution. The identification is uncertain to the extent of the number of H atoms in  $\text{C}_4\text{SiH}_x^-$  where  $x = 0-4$ .

mass spectrometer to distinguish between reactant and product  $\text{H}^-$  ions so that the analogous reaction involving  $\text{D}^-$ , viz.,



was investigated instead.  $\text{CH}_4$  was added into a flowing  $\text{CD}_4$ -He plasma containing  $\text{D}^-$ . The results of such an experiment are shown in Figure 5. The  $\text{D}^-$  ions are not depleted nor are  $\text{H}^-$  ions produced as the  $\text{CH}_4$  is added. These results provide an upper limit for  $k_{12}$  of  $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

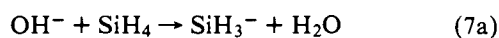
$\text{H}^- + \text{CD}_4$ . In the studies of the reaction of  $\text{D}^-$  with  $\text{SiH}_4$ , the  $\text{D}^-$  ions were produced from  $\text{CD}_4$  which was added upstream of the electron gun and was therefore also present in the reaction region. The  $\text{H}^-$  produced by reaction 5a therefore could have reacted with  $\text{CD}_4$  by displacement according to:



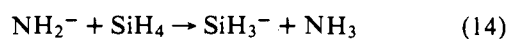
At the  $\text{CD}_4$  flows used in these experiments ( $\sim 2 \times 10^{18} \text{ molecules s}^{-1}$ ) the rapid occurrence of reaction 13 would have been manifested by the appearance of appreciable curvature in the  $\text{D}^-$  decay. No such curvature is evident in Figure 2. From this qualitative observation we estimate that  $k_{13} \leq 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## Discussion

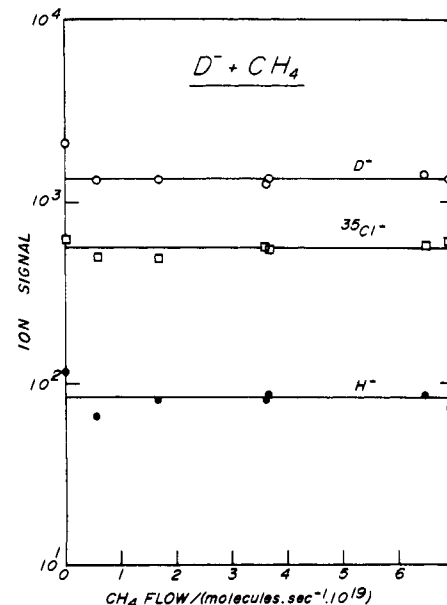
The reactions of anions with  $\text{SiH}_4$  and  $\text{CH}_4$  have not been studied extensively by experiment in the past. Brauman and co-workers<sup>23</sup> have reported the observation of the proton transfer reactions:



and



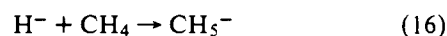
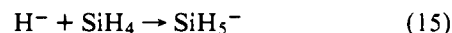
For both of these reactions their ion-cyclotron-resonance measurements implied a preferred direction for proton transfer as indicated. There was apparently no evidence for the occurrence of a displacement leading to the formation



**Figure 5.** A study of the displacement of  $\text{H}^-$  in  $\text{CH}_4$  by  $\text{D}^-$ . Methane is added to a flowing  $\text{CD}_4$ -He plasma:  $T = 298 \text{ K}$ ,  $P = 0.359 \text{ Torr}$ ,  $\text{CD}_4$  flow =  $1.39 \times 10^{18} \text{ molecules s}^{-1}$ ,  $L = 85 \text{ cm}$ , and  $\bar{v} = 8.1 \times 10^3 \text{ cm s}^{-1}$ .

of  $\text{H}^-$ . Brauman and co-workers also did not report the observation of channel 7b nor did they measure rate constants for reactions 7a and 14. The reactions of  $\text{OH}^-$ ,  $\text{C}^-$ ,  $\text{C}_2^-$ , and  $\text{C}_2\text{H}^-$  with  $\text{CH}_4$  have been investigated previously<sup>21</sup> with the flowing afterglow technique which allowed the determination of the upper limits to the total specific rates of reaction of these anions with  $\text{CH}_4$  which are indicated in Table II.

**Comparisons with Theoretical Predictions.** The ab initio quantum mechanical calculations for reactions of anions with  $\text{SiH}_4$  and  $\text{CH}_4$  have been restricted to hydride ion attack. They have been concerned principally with the evolution of the geometry, energy, and electronic structure of the reacting species in their formation of the intermediates  $\text{SiH}_5^-$  and  $\text{CH}_5^-$ , viz., along the reaction paths:



The observations reported here for the  $\text{H}^-$  and  $\text{D}^-$  reactions allow an experimental assessment of the energies of the intermediates or the energy barriers along the reaction paths predicted by these calculations.

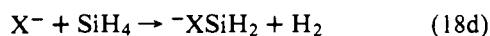
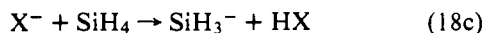
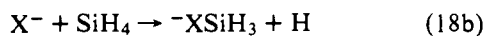
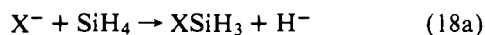
The calculations of Wilhite and Spialter<sup>4</sup> predict that the gas-phase reaction (eq 15) proceeds via attack of the hydride ion on a face of the tetrahedron of silane with an energy barrier of  $8.6 \text{ kcal mol}^{-1}$  yielding a trigonal bipyramidal form of  $\text{SiH}_5^-$  that is  $16.93 \text{ kcal mol}^{-1}$  stable with respect to the separated reactants. The energy difference is calculated to be  $-18.6 \text{ kcal mol}^{-1}$  by Baybutt.<sup>2</sup> Our experimental results are in accord with a lower energy for the  $\text{SiH}_5^-$  intermediate but do not corroborate the prediction of a large reaction barrier for the  $\text{H}^-$  attack. A comparison of  $k_5$  determined in this study with the capture rate constant which can be calculated from the classical Langevin theory of ion molecule collisions<sup>17</sup> indicates that at least six out of ten collisions of  $\text{D}^-$  with  $\text{SiH}_4$  lead to reaction.<sup>24</sup> Thus it appears that reaction 15 proceeds with little or no activation energy.<sup>25</sup> The magnitude of this activation energy,  $E_a$ , can be estimated<sup>27</sup> in the traditional Arrhenius manner according to

$$k_{\text{exptl}} = k_c e^{-E_a/RT} \quad (17)$$

where  $k_{\text{exptl}}$  is the measured and  $k_c$  is the capture rate constant.<sup>21</sup> Equation 17 yields a value for  $E_a \approx 0.3 \text{ kcal mol}^{-1}$  which, as a result of the oversimplification introduced by eq 17, must be regarded as an upper limit.<sup>21</sup> An activation energy of  $8.6 \text{ kcal mol}^{-1}$  would result in a value for  $k_5 \sim 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The discrepancy between theory and experiment for the activation energy of reaction 15 probably reflects a deficiency in the theory—either a lack of proper polarizing functions (the ab initio calculations by Wilhite and Spialter<sup>4</sup> did not include p-type basis functions on the hydrogens) or perhaps an incorrect approach geometry.

The many calculations<sup>2,4,5,7-10</sup> of portions of the potential energy surface of reaction 16 all predict a much higher energy for the reaction intermediate  $\text{CH}_5^-$  than the separated reactants  $\text{H}^- + \text{CH}_4$ . For example, Dedieu and Veillard<sup>5</sup> calculated a difference of  $60.2 \text{ kcal mol}^{-1}$ . This result is in complete accord with our room temperature measurements of eq 12 and 13 which indicate an activation energy which may be at least as large as  $6 \text{ kcal mol}^{-1}$ .

**Competition between Product Channels.** The quantum mechanical calculations reported for reactions of anions with  $\text{SiH}_4$  and  $\text{CH}_4$  have as yet not been extended to include product channels other than  $\text{H}^-$  displacement. However, the observations reported in this study for the reactions of anions with  $\text{SiH}_4$  demonstrate that  $\text{H}^-$  displacement often proceeds in competition with alternate product channels. The channels observed with the nucleophiles  $\text{X}^- = \text{H}^-, \text{D}^-, \text{OH}^-, \cdot\text{C}^-, \cdot\text{C}_2^-, \text{and } \cdot\text{C}_4^-$  include hydride ion displacement (18a), hydrogen atom displacement (18b), proton transfer (18c), and hydrogen elimination (18d):



For most of the nucleophiles investigated at least two of these four channels were observed to be competing with each other. For example, although  $\text{D}^-$  reacted with  $\text{SiH}_4$  predominantly by  $\text{H}^-$  displacement, a portion of the reactive collisions resulted in the transfer of a proton. For the reaction of  $\text{OH}^-$  with  $\text{SiH}_4$ , competition was observed between channels 18c and 18d.

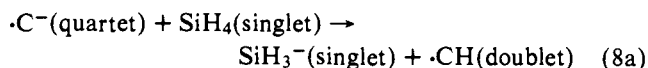
The  $\text{H}^-$  displacement channel is often excluded on thermodynamic grounds. For this channel to be exothermic, the following condition must be satisfied:

$$D(\text{SiH}_3\text{-X}) > D(\text{SiH}_3\text{-H}) + \text{EA}(\text{X}) - \text{EA}(\text{H}) > 63 \text{ kcal mol}^{-1} + \text{EA}(\text{X})$$

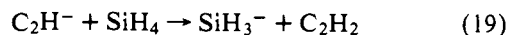
where the bond dissociation energy  $D(\text{SiH}_3\text{-H}) \approx 80 \text{ kcal mol}^{-1}$  and  $\text{EA}(\text{H}) = 17.4 \text{ kcal mol}^{-1}$ .<sup>28,29</sup> The electron affinities of the species X used in this study are generally at least  $25 \text{ kcal mol}^{-1}$  and as large as  $83 \text{ kcal mol}^{-1}$ . Although the values for  $D(\text{SiH}_3\text{-X})$  are generally not known, they are unlikely to be large enough to compensate for this high electron affinity of X. The  $\text{H}^-$  displacement channel is therefore likely to be thermodynamically unfavorable and any reaction of the anion with  $\text{SiH}_4$  will proceed via other channels as was observed to be the case for the reactions of  $\text{OH}^-, \cdot\text{C}^-, \cdot\text{C}_2^-, \text{and } \cdot\text{C}_4^-$ .

The reaction of  $\cdot\text{C}^-$  with  $\text{SiH}_4$  was observed to proceed only via proton transfer which may be exothermic by as much as  $\sim 4 \text{ kcal mol}^{-1}$  according to the recent determination of  $\text{EA}(\text{SiH}_3) \leq 1.44 \pm 0.03 \text{ eV}$ .<sup>30</sup> The reaction is, however, unusually slow as proton transfer in the gas phase generally proceeds on nearly every collision.<sup>31</sup> In fact, this is

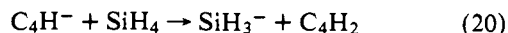
one of the slowest exothermic proton transfer reactions observed to date. We suggest that the relative inefficiency of this reaction may be attributed to the violation of spin conservation which is involved:



Other exothermic proton transfer reactions involving  $\cdot\text{C}^-(^4\text{S})$  have been observed to be slow<sup>31</sup> and indeed are expected to be slow for the same reason. Our measurements also indicate that the proton transfer reactions:

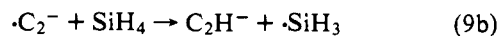


and



proceed extremely slowly in spite of the fact that  $\text{SiH}_4$  is a much stronger acid than  $\text{C}_2\text{H}_2$  and probably also  $\text{C}_4\text{H}_2$ . We cannot explain this result.

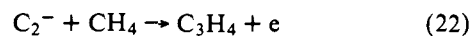
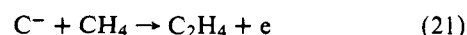
When the species  $\text{X}^-$  is a radical, then H atom displacement becomes a viable alternate channel since  $\text{XSiH}_3$  is not likely to have a significant electron affinity. This is evidenced by the production of  $\text{C}_2\text{SiH}_3^-$  and  $\text{C}_4\text{SiH}_3^-$  observed in these experiments as a result of the reactions with  $\text{SiH}_4$  of the radical anions  $\cdot\text{C}_2^-$  and  $\cdot\text{C}_4^-$ , respectively. The carbon analogues, viz.,  $\text{C}_3\text{H}_3^-$  and  $\text{C}_5\text{H}_3^-$ , have been observed to be stable in the gas phase. H-Atom transfer is another channel which, although not observed in these experiments, should be considered when  $\text{X}^-$  is a radical. For example, the reaction



is exothermic by  $\sim 25 \text{ kcal mol}^{-1}$  and therefore thermodynamically favorable.

The nonreactivity of  $\text{CH}_4$  towards anions, which is immediately evident from an inspection of Table II, contrasts the reactivity generally observed for  $\text{SiH}_4$  towards the same anions. This striking difference in reactivity can, however, be rationalized simply in terms of the thermodynamics of these systems. A thermodynamic analysis of channels 18a to 18d for  $\text{CH}_4$  indicates that all of these channels are in fact endothermic for  $\text{X}^- = \text{OH}^-, \cdot\text{C}^-, \cdot\text{C}_2^-, \text{and } \text{C}_2\text{H}^-$  so that they are not expected to proceed rapidly at the temperature of these experiments.

A number of associative detachment channels resulting in the "insertion" of  $\text{C}_x\text{H}_y^-$  are thermodynamically accessible to the reactions of  $\cdot\text{C}^-, \cdot\text{C}_2^-, \text{and } \text{C}_2\text{H}^-$  with  $\text{CH}_4$  at 300 K, for example:<sup>21</sup>



Analogous reactions are presumably also thermodynamically allowed in the case of  $\text{SiH}_4$ . However, in both cases, constraints introduced by the required breaking and making of bonds are likely to lead to activation energy barriers of sufficient magnitude to prevent their observation at room temperature.<sup>21</sup>

**Acknowledgments.** We thank Dr. Baybutt for communicating to us the results of his calculations for the reactions of  $\text{H}^-$  with  $\text{SiH}_4$  and  $\text{CH}_4$  and for suggesting their comparison with experimental observations. We also thank the reviewer who provided useful comments regarding possible deficiencies in the ab initio calculations on  $\text{SiH}_4 + \text{H}^-$  by Wilhite and Spialter.<sup>4</sup> The financial support of the National

Research Council of Canada and the Sloan Foundation is gratefully acknowledged.

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- (25) An energy barrier of 8.6 kcal mol<sup>-1</sup> should, at the thermal energies of these experiments, give rise to an activation energy >8.6 kcal mol<sup>-1</sup>.<sup>26</sup>
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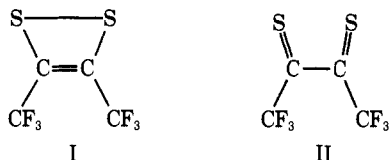
# Molecular Structure of 1,2-Bis(trifluoromethyl)dithiete by Vapor Phase Electron Diffraction

J. Lawrence Hencher,\* Quang Shen, and Dennis G. Tuck

Contribution from the Department of Chemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada. Received March 10, 1975

**Abstract:** The molecular structure of 1,2-bis(trifluoromethyl)dithiete has been determined in the vapor phase by electron diffraction. The results confirm the dithiete structure, in which the principal geometrical parameters, based on  $C_2$  symmetry, are:  $r_g(C-F) = 1.326 \pm 0.003$ ,  $r_g(C=C) = 1.40 \pm 0.03$ ,  $r_g(C-C) = 1.50 \pm 0.01$ ,  $r_g(S-C) = 1.73 \pm 0.01$ ,  $r_g(S-S) = 2.05 \pm 0.01$  Å;  $\angle(C=C-S) = 100.8 \pm 0.6$ ,  $\angle(C=C-C) = 122.9 \pm 0.7$ ,  $\angle(F-C-C) = 110.8 \pm 0.6^\circ$ . The rotational parameter  $\tau(S-C-C-S) = 0.4 \pm 3.4^\circ$  indicates no significant deviation from planarity in the  $C_2S_2$  ring excluding shrinkage effects which were not included in the analysis. The  $CF_3$  groups are semistaggered, rotated about the C—C bonds by  $34 \pm 6^\circ$  relative to planar trans F—C—C=C. The quoted uncertainties represent the estimated limits of experimental errors. A comparison with other structures suggests delocalization of the carbon-carbon  $\pi$  system to include the sulfur atoms, but without appreciable participation of the S—S bond.

1,2-Bis(trifluoromethyl)dithiete was the first compound synthesized in which the unusual dithiete ring<sup>1</sup> could be postulated. Infrared and <sup>19</sup>F NMR spectra<sup>2</sup> revealed the presence of a C=C bond, and showed that the  $CF_3$  groups are attached to a doubly bonded carbon atom, but the red color of the compound prevented any observation of the sulfur-sulfur vibrations by Raman spectroscopy. Simple molecular orbital calculations<sup>3</sup> showed that structure (I), involving a dithiete ring, is more stable than the acyclic dithione structure (II).



The title compound has been extensively used in the preparation of dithiolene complexes of a number of transition and main group metals.<sup>4</sup> It is apparent that in all of these complexes, ring opening allows the 1,2-bis(trifluoromethyl)dithiete to act as a bidentate ligand, and a number of x-ray crystallographic structure studies of compounds with transition metal ions have been reported (see below). We have now determined the structure of the par-

ent compound in the vapor phase by electron diffraction, and find that I is indeed the correct formulation under these experimental conditions.

## Experimental Section

A sample of 1,2-bis(trifluoromethyl)dithiete, kindly provided by Dr. A. T. Berniaz of Simon Fraser University, showed no impurity bands in its infrared spectrum and was used without further purification.

Sector electron diffraction patterns were recorded on the University of Windsor apparatus<sup>5</sup> on Kodak 4 × 5 in. electron image plates. The experimental conditions for the dithiete exposures are presented in Table I. In each experiment, separate  $CS_2$  patterns were recorded for the  $s$  scale calibration using the standard  $CS_2$  structural parameters reported by Kuchitsu<sup>6</sup> ( $s = (4\pi/\lambda) \sin(\theta/2)$ ;  $\lambda$  = electron wavelength;  $\theta$  (diffraction angle) =  $\tan^{-1}(r/L)$  where  $r$  is the radius and  $L$  is the camera length).

The optical densities of the experimental plates were sampled at 0.1095 mm intervals with the microdensitometer<sup>5</sup> described previously, with the plate spinning and moving continuously so that an annular portion, 0.075 mm, of the plate was sampled in each of 350 measurements obtained for the radial range  $0.75 < r < 4.5$  cm. Interpolation of densities at  $\pi/10$  intervals in  $s$  (by the Lagrange method) was based on six points for long camera plates, and three points for short camera plates. The interpolated optical densities were converted to relative intensities by the correction<sup>7</sup>