J. Am. Chem. Soc. **1993**, *115*, 1998-2005

Gas-Phase Chemistry of $HSiS^-$ and $HSiNH^-$: Ions Related to Silathioformaldehyde and the Silaazomethine of Formaldehyde

Robert Damrauer,* Michèle Krempp, and Richard A. J. O'Hair

Contribution from the Department of Chemistry, University of Colorado at Denver, P.O. Box 1733364, Denver, Colorado 80217-3364, and Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, Colorado 80309-0215. *Received July 20, 1992*

Abstract: Anions related to silathioformaldehyde ($H_2Si{=}S$) and the silaazomethine of formaldehyde ($H_2Si{=}NH$) have been prepared and studied using flowing afterglow selected ion flow tube techniques. The connectivities of these anions are shown in experimental studies to be $[HSiS]^-$ and $[HSiNH]^-$. In addition, ab initio computational studies demonstrate that these are the most stable anion isomers. These anions are prepared by both collisionally-induced dissociation and direct source reactions. The anions resulting from the later preparations have been submitted to reaction chemistry studies with CO_2, COS, CS_2, SO_2, O_2, and C_6F_6. Comparisons with earlier studies of $HSiO^-$ are made in terms of a simple mechanistic picture.

Introduction

Low-valent silicon-containing compounds have been widely studied in recent years both experimentally[1,2] and computationally.[3] Studies of silicon–carbon, silicon–oxygen, silicon–nitrogen, and silicon–silicon multiply bonded compounds have demonstrated that such species are generally stable, but are highly reactive unless encumbered by sterically demanding substituents.[1] Although our understanding of such species has certainly increased in recent years, our knowledge is still primative compared to that accumulated over the years on analogous carbon species.

We have been interested in low-valent silicon-containing species for some time and have used ion–molecule reaction chemistry to study simple silicon-containing anions whose conjugate acids are highly reactive, low-valent silicon-containing neutrals.[4-8] Our previously reported work has concentrated on anions (conjugate bases) of $(CH_3)_2Si$,[4] $(CH_3)_2Si{=}CH_2$,[5] $Si{=}CH_2$,[6] $H_2Si{=}O$,[7] $CH_3(H)Si{=}O$,[8] and $CH_3O(H)Si{=}O$.[8] These studies have the advantage that many simple silicon-containing anions are readily prepared in the gas phase, even though their conjugate acids would be expected to be exceptionally reactive in either the gas or condensed phase. Thus, in studying the reaction chemistry of simple anions unencumbered by bulky substituents in the gas phase, we have not only a measure of the reactivity of such anions, but an indirect probe of their corresponding conjugate acids.

The flowing afterglow selected ion flow tube (FA-SIFT) technique which we use allows the selection of ions from complex reaction mixtures.[6,9] Because reaction chemistry studies occur under single-collision conditions, stoichiometric relationships can be determined (excluding, of course, the many collisions that ions and neutrals undergo with neutral buffer gas; see Experimental Section). In addition, we can measure reaction rates and detect multiple reaction pathways. In favorable cases, thermochemical properties such as heats of formation of anions and their corresponding conjugate acids, electron affinities of corresponding radicals, and gas-phase acidity of the conjugate acids can be determined as well.[7] In relating the chemistry of anions and their conjugate acid species, it is important to realize that the structure of the acid is not always known. For example, the conjugate acid of the anionic species containing two hydrogens, one silicon, and one carbon (designated $[H_2, Si, C]$; see note at the end of paragraph) could be either $HC{\equiv}SiH$, $H_2C{=}Si$, or $C{=}SiH_2$. When we study the reactions of $[H, Si, C]^-$ with acids, we are uncertain of the structure of the reaction product with acids unless other information is available. Thus, linking our experimental studies with computational work carried out both by other workers[10] and us[7] has proven advantageous in sorting out structural questions for such species. (General formulations like $[H_2, Si, C]$ and $[H, Si, C]^-$ will be used for compounds and anions whose compositions are known, but whose structures are not. When the structure is known, the connectivity of its atoms will be clearly designated. For example, the $[H_2CSi]$ formulation indicates that two hydrogens are bound to carbon which is bonded to silicon. Similarly, $[HSiO]^-$ represents a typical anion where the negative charge location is unknown, but the connectivity is. $HSiO^-$ indicates known connectivity with negative charge localization on oxygen.)

In this paper we describe experimental and computational studies on $[H, Si, S]^-$ and $[H_2, Si, N]^-$. These studies are summarized in the context of our more general work on the anions $[H_n, Si, X]^-$ and the parent conjugate acid compounds $[H_{n+1}, Si, X]$, where we have now studied X = C for $n = 1$,[6] X = O for $n = 1$,[7] X = S for $n = 1$, and X = N for $n = 2$. The work on the structure and reactivity of the two anions and their conjugate acids discussed herein further probes the relationship between silicon and carbon (in these cases between the silicon analogues of thioformaldehyde and azomethine).

Experimental Section

All experiments were carried out at room temperature in the flowing afterglow selected ion flow tube (FA-SIFT). Although this instrument has been described in detail previously,[11] a brief summary of its operation in these experiments is appropriate for readers who are not familiar with the technique. The FA-SIFT consists of four sections: a flow tube for ion preparation (A), an ion separation and purification region (B), a second flow tube for studying the chemical reactions of the ions selected (C), and finally an ion detection region (D). In the first flow tube (A), for example, ions like HS^- (prepared from HO^- and CS_2) or H_2N^- (prepared by electron impact of NH_3) are entrained in a rapidly flowing helium stream (0.3 Torr). Phenylsilane is added downstream through a movable inlet producing the major products shown in eq 1 and 2.

$$C_6H_5SiH_3 + HS^- \longrightarrow H_3SiS^- + C_6H_6 \tag{1}$$

$$C_6H_5SiH_3 + H_2N^- \longrightarrow H_3SiNH^- + C_6H_6 \tag{2}$$

---

* Address correspondence to this author at the University of Colorado at Denver.

[1] Raabe, G.; Michl, J. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1989; pp 1015–1142. This review gives an excellent collection of relevant silicon references up through early 1989.

[2] O'Hair, R. A. J.; Krempp, M.; Damrauer, R.; DePuy, C. H. *Inorg. Chem.* **1992**, *31*, 2092–6. This paper gives a collection of relevant references for other than silicon low-valent species.

[3] Apeloig, Y. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1989; pp 57–225.

[4] Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* **1986**, *5*, 2054–7.

[5] Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J. *Organometallics* **1986**, *5*, 2050–4.

[6] Damrauer, R.; DePuy, C. H.; Barlow, S. E.; Gronert, S. *J. Am. Chem. Soc.* **1988**, *110*, 2005–6.

[7] Gronert, S.; O'Hair, R. A. J.; Prodnuk, S.; Sülzle, D.; Damrauer, R.; DePuy, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 997–1003.

[8] Damrauer, R.; Krempp, M. *Organometallics* **1990**, *9*, 999–1004.

[9] Damrauer, R.; Krempp, M.; Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2393–2400.

[10] Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 5244–8.

[11] Van Doren, J. M.; Barlow, S. E.; Depuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 85–100.

0002-7863/93/1515-1998$04.00/0 © 1993 American Chemical Society

At the end of the first flow tube, the ions are sampled through a 2-mm orifice into the ion separation region (B), and the helium and other neutrals are removed by pumping while the ions are focused into a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole can be tuned to *m*/*z* 46 or 63 to inject H_3SiNH^- or H_3SiS^- into the second flow tube (C) where they are again entrained in helium (0.5 Torr) and undergo reaction. At the end of the second flow tube, the requisite ion is sampled through a 0.5-mm orifice and detected by an electron multiplier. We have previously reported[12] the preparation of H_3SiS^-; its reaction chemistry and that of H_3SiNH^- will be reported in detail later.

To inject ions from the low-pressure (10^{-6} Torr) region of the SIFT quadrupole into the higher pressure region of the second flow tube, they must be extracted by an electrical potential. While this potential imparts kinetic energy to the ions, they are generally relaxed by multiple collisions with the helium buffer gas. If this potential is made sufficiently high, some ions can be induced to undergo collisionally-induced dissociation (CID) to form new ions.[7,9] For example, both the *m*/*z* 46 and 63 ions are transformed into ions of *m*/*z* 44 and 61, respectively. These ions are formulated as shown in eq 3 and 4. Notice that a second anionic product forms in reaction 3. To overcome any potential problems involving additional products, we have prepared *m*/*z* 44 and 61 ions directly in the first flow without a separate CID step. Thus, NH_2^-, SiH_4, and CS_2 give $[HSiS]^-$, and H_2N^- and $C_6H_5SiH_3$ give $[HSiNH]^-$. These direct routes have been used in most of the reactions reported here. The connectivity of $HSiNH^-$ is based on CID experiments of D_3SiNH^- in which only $DSiNH^-$ is observed. Such CID experiments are related to high-energy CID studies carried out by Bowie and co-workers.[13]

$$H_3SiS^- \xrightarrow{\text{CID}} [HSiS]^- + H_2 \tag{3a}$$

$$\phantom{H_3SiS^- \xrightarrow{\text{CID}}} \to HS^- + H_2Si \tag{3b}$$

$$H_3SiNH^- \xrightarrow{\text{CID}} [HSiNH]^- + H_2 \tag{4}$$

All reactions were studied at 300 K at a helium buffer gas pressure of 0.5 Torr and a flow of ~225 STP $cm^3\ s^{-1}$. Branching ratios were determined as a function of reaction distance and are reported as extrapolations to zero reaction distance to eliminate any effects of differential diffusion among the ions and of secondary reactions. Branching ratios were also corrected for mass discrimination in the detection region by directly measuring the detector response as a function of ion current at the nose cone orifice. Rate coefficients were determined under pseudo-first-order conditions by monitoring the reactant ion density as a function of reaction distance (which is proportional to time) using a measured flow of the neutral reagent. Reported values are the average of three measurements using different reagent flows and are reproducible to within ±10%.

Gases were obtained from commercial sources and were of the following purities: He (99.995%), N_2O (99.99%), O_2 (99.95%), CH_4 (99.99%), NH_3 (99.99%), CO_2 (99.5%), SO_2 (99.9%), COS (97.7%), and SiH_4 (99.995%). Other reagents also were obtained from commercial sources. The helium buffer gas was passed through a liquid-nitrogen-cooled molecular sieve trap before entering the flow tubes.

Structures were optimized at the Hartree–Fock level using Gaussian 90[14] with a 6-31++G(d,p) basis set. All structures were verified as minima on the potential energy surface by carrying out vibrational frequency analyses using the same basis set. The resulting frequencies and zero-point energies were scaled by 0.9. In addition, single-point energies at the MP2/6-31++G(d,p)//HF/6-31++G(d,p) level were calculated for each species.

Results and Discussion

Two new low-valent silicon systems are considered here, namely, $[H_2, Si, S]/[H, Si, S]^-$ and $[H_3, Si, N]/[H_2, Si, N]^-$. Their experimental and computational characteristics will be compared with two previously described systems, namely, $H_2SiO/HSiO^-$[7] and $SiCH_2/HCSi^-$.[6] Although silicon in $SiCH_2/HCSi^-$ has an oxidation level different from those in the other three systems, it offers an interesting opportunity for comparison. In the sections which follow, we will review the computational results on neutral species related to the anions studied here. We will present new computational and experimental results which characterize these anions. The experimental studies of these anions consider their gas-phase acidities, their reactivity with representative neutral reagents, and the thermochemical consequences of these results as well as reactivity comparisons of various low-valent anions.

Computational Comparisons of Neutral Components. The neutral components of the four systems just mentioned have been studied computationally by a number of workers. These studies tend to focus on the structure and energy of the various isomeric low-valent silicon species. Thus, questions regarding bonding preferences in these silicon compounds naturally arise. Perhaps the major point addressed in such computational studies is the tendency of silicon to make multiple bonds, especially in cases where alternative bonding possibilities exist.

A number of computational studies have established that H_2CSi is the most stable $[H_2, Si, C]$ isomer.[15] The lowest energy structure of H_2CSi is a singlet ($^1A_1$) with C_{2v} symmetry.[15] At the MP4/SDTQ/6-31(d) level, the relative energy difference between this $^1A_1$ structure and its nearest energy isomer, which is a triplet ($^3A_2$) with C_{2v} symmetry, is 36 kcal/mol. The lowest energy HCSiH isomer is 61 kcal/mol above the $^1A_1$ structure.

In contrast, the relative energy difference between the isomers of $[H_2, Si, O]$ is very small. Nagase and co-workers have shown that the silylene, HSiOH (trans), is more stable than the silanone, H_2SiO, by about 2 kcal/mol at the CI(S+D+QC)/6-31G(d,p)//6-31G(d) level.[16] At the MP4/MC-311G(d,p) level, however, Gordon indicates that H_2SiO is more stable than HSiOH (trans) by about 3 kcal/mol.[7]

The silathione, H_2SiS, is suggested by Nagase and co-workers to be 9 kcal/mol more stable than its silylene isomer, HSiSH, at a comparable computational level.[17] Thus, although the energies for the oxygen isomers are very nearly equal, the double-bonded isomer is slightly favored over the silylene. This difference is more pronounced in the related sulfur case.

Calculations by Truong and Gordon on $[H_3, Si, N]$ suggest that the silylene isomer, H_2NSiH, is 18 kcal/mol more stable than the azomethine isomer, $HNSiH_2$, at the MP4/MC-311G(d,p) level.[18] Recent argon matrix isolation studies have identified H_2NSiH as a stable molecule.[19]

The importance of silylene structures has been amply demonstrated for a number of neutral silicon compounds.[3] While the results reviewed above appear to show no clear trends at first glance, the stabilization of the silylene structures is actually dominant. Indeed, both the carbon and nitrogen examples show the silylene form to be favored over other possible structures. In the oxygen and sulfur cases, the double-bonded isomer is more stable, but by a surprisingly small amount given that for the carbon analogues of each of these cases, namely, $HC{\equiv}CH/H_2C{=}C$, $H_2C{=}O/HCOH$, $H_2C{=}S/HCSH$, and $H_2C{=}NH/HCNH_2$, the multiply bonded isomer is strongly favored over its carbene isomer.[3]

Computational Comparisons of Anionic Components. Computational studies of the anions under study are an important adjunct to a complete analysis of their flowing afterglow reactivity. We have, thus, carried out ab initio computations[14] on $[H, Si, S]^-$ and $[H_2, Si, N]^-$. These will be compared with studies of $[H, Si, C]^-$ and $[H, Si, O]^-$ which were reported earlier.[6,7] More detailed computational work which will consider the reaction dynamics of these anions will be published in the future.[20]

---

(12) (a) Sheldon, J. C.; Bowie, J. H.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 6794–6800. (b) O'Hair, R. A. J.; Sheldon, J. C.; Bowie, J. H.; Damrauer, R.; Depuy, C. H. *Aust. J. Chem.* **1989**, *42*, 489–96.

(13) See: O'Hair, R. A. J.; Ph.D. Thesis, University of Adelaide, 1989, for high-energy CID of $RSiD_2NH^-$ species. For other high-energy CID of silicon-containing anions, see: O'Hair, R. A. J.; Bowie, J. H.; Currie, G. J. *Aust. J. Chem.* **1988**, *41*, 57–67.

(14) Gaussian, 90, Revision J.; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1990.

(15) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270–284. Other important earlier references are given in this paper.

(16) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833–2840.

(17) Kudo, T.; Nagase, S. *Organometallics* **1986**, *5*, 1207–1215.

(18) Truong, T. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1775–1778.

(19) Maier, G.; Glatthaar, J.; Reisenauer, H. P. *Chem. Ber.* **1989**, *122*, 2403–2405.

Table I. Calculated Energies, Geometries, and Vibrational Frequencies of $[H,Si,S]^-$, $[H_2, Si,N]^-$ and $[H,Si,O]^-$ Isomers at the MP2/6-31++G (d,p)//6-31++G (d,p) Level

anion	energy[a] (hartrees)	rel energy (kcal/mol)	zero-point energy (scaled by 0.9) (hartrees)	corrected frequencies (cm^{-1})	geometry (Å and deg)	
$HSiS^-$	−687.233 262	0	0.006 965	566, 767, 1724	Si–S	2.045
					Si–H	1.548
					H–Si–S	103.7
^-SiSH	−687.161 388	45.1	0.008 137	373, 718, 2480	Si–S	2.219
					S–H	1.336
					Si–S–H	106.2
$HSiNH^-$ (trans)	−344.742 055	0	0.018 976	713, 777, 874, 929, 1696, 3339	Si–H	1.553
					Si–N	1.650
					N–H	1.006
					H–Si–N	102.6
					Si–N–H	111.5
$HSiNH^-$ (cis)	−344.740 323	1.1	0.018 411	648, 739, 866, 935, 1537, 3358	SiH	1.590
					Si–N	1.646
					N–H	1.005
					H–Si–N	105.5
					Si–N–H	118.2
$[H_2SiN]^-$	−344.704 340	23.7	0.016 038	475, 634, 996, 1076, 1895, 1964	SiH	1.506
					Si–N	1.581
					H–Si–N	128.2
$[SiNH_2]^-$	−344.703 172	24.4	0.023 586	458, 698, 773, 1542, 3408, 3475	Si–N	1.764
					N–H	0.996
					Si–N–H	123.8
					H–N–H	112.4
$HSiO^-$	−364.630 539	0	0.007 613	801, 1045, 1495	H–Si	1.599
					Si–O	1.550
					H–Si–O	106.8
^-SiOH	−364.563 559	42.0	0.012 181	668, 857, 3822	Si–O	1.721
					O–H	0.939
					Si–O–H	111.6

[a] See Experimental Section for computational details.

Computations by Schmidt and Gordon[10] show that the $[HCSi]^-$ isomer is strongly favored over $[CSiH]^-$. This structure also best fits the reaction chemistry of the ion. In a series of reactions with neutral molecules possessing polar reaction centers, we have suggested that $[HCSi]^-$ reacts as a carbon nucleophile.[6]

Previously reported computations at the MP2/6-31++G(d,p)//HF/6-31++G(d,p) level with zero-point corrections scaled by 0.9 show that $[HSiO]^-$ is more stable than $[HOSi]^-$ by about 42 kcal/mol.[7,21] Formulation of this anion as $HSiO^-$ allowed us to rationalize its chemical behavior. This structure also takes account of the large electronegativity difference between silicon and oxygen.

In the present study, MP2/6-31++G(d,p)//HF/6-31++G(d,p) level computations with zero-point corrections scaled by 0.9 on both $[H, Si, S]^-$ and $[H_2, Si, N]^-$ give the results summarized in Table I. These demonstrate the similarity of $[H, Si, S]^-$ and $HSiO^-$. Thus, the $[HSiS]^-$ isomer is some 45 kcal/mol more stable than $[SiSH]^-$. The H—Si—S bond angle of 104° is close to the H–Si–O angle of 107° reported earlier as are the corresponding Si–H bond lengths (1.55 and 1.60 Å, respectively). We have not investigated the charge distribution in this anion but, because of the electronegativity difference between silicon and sulfur, suggest a silylene formulation of $HSiS^-$. This is consistent with the reaction chemistry this anion undergoes.

The $[H_2, Si, N]^-$ computations show that trans $[HSiNH]^-$ is slightly more stable than its cis isomer (1 kcal/mol), but considerably more so than either $[H_2SiN]^-$ (24 kcal/mol) or $[SiNH_2]^-$ (24 kcal/mol) (Table I). Geometry effects in the trans and cis isomers show that, while both are planar and of very similar energy, the bond lengths and angles are surprisingly different (Si–H bond: trans = 1.55 Å; cis = 1.59 Å) (H—N—Si angle: trans = 112°; cis = 118°). The increase of the cis H—N—Si angle presumably compensates for unfavorable nonbonding interactions between cis hydrogens caused by lengthening of the cis Si–H bond.

Table II. Bracketing Studies of $HSiS^-$ and $HSiNH^-$

anion	reference acid	$\Delta G°$ acid[a] (kcal/mol)	bracket[b]
$HSiS^-$	CH_3CO_2H	341.5 ± 1.9	−
$HSiS^-$	HCO_2H	338.2 ± 1.9	−
$HSiS^-$	HCl	327.9 ± 0.2	+
$HSiS^-$	CHF_2CO_2H	323.6 ± 1.9	+
$HSiNH^-$	CH_3COCH_3	358.7 ± 1.9	−
$HSiNH^-$	CF_3CH_2OH	354.2 ± 1.9	−
$HSiNH^-$	pyrrole	350.9 ± 1.9	+
$HSiNH^-$	CH_3SH	350.6 ± 1.9	+

[a] The free-energy change, $\Delta G°_{acid}$, is commonly referred to as the acidity. The acidity values reported are determined in relative terms, and their ordering with the bracketing reference acids is known precisely. In absolute terms, the acidities depend on how accurately the acidities of the reference acids are known. This, of course, varies with the experimental method used in their determination. As a result, it is difficult to provide error limits on the accuracy of the data which are universally accepted. We estimate that a ±4 kcal/mol absolute error limit is consistent with our methodology and the reference acids used by us. [b] A "+" in the bracket column signifies that the reference acid reacts with the corresponding anion giving the neutral, silicon-containing species (see text) and the M − 1 of the reference acid; a "−" signifies that the acid listed does not react with the corresponding anion.

Experimental verification of the connectivity for $[HSiNH]^-$ rests on several observations. As indicated earlier (see Experimental Section), CID of D_3SiNH^- gives only $[DSiNH]^-$. In addition, $[HSiNH]^-$ reacts with both CD_3OD and CH_3CH_2OD to give $[HSiND]^-$, while $[DSiNH]^-$ gives no exchange with CH_3CH_2OH while giving $[DSiND]^-$ with CH_3CH_2OD.

Consideration of both the reactivity (vide infra) and the greater electronegativity of sulfur and nitrogen with respect to silicon suggests that the charge be concentrated on sulfur as $HSiS^-$ and nitrogen as $HSiNH^-$. Such a formulation as well as that previously

---

(20) A number of related computational studies are underway including barrier computations for proton transfer to $HSiX^-$ species and hydride transfers from them: O'Hair, R. A. J.; Gordon, M. S.; Damrauer, R.

(21) A close examination of the energies of $HSiO^-$ reported here and in ref 7 shows that they are not identical. This results because the previous energy calculations at the MP2/6-31++G(d,p)//HF/6-31++G(d,p) level included the core electrons, while the results presented here do not. Since the relative energies of the two $[H,Si,O]^-$ isomers are identical in either case, we have carried out the single-point energy calculations for the isomers of $[H,Si,S]^-$ and $[H_2,Si,N]^-$ without considering the core electrons.

Table III. Products, Branching Ratios, Rates Coefficients, and Efficiencies of $HSiS^-$ Reactions

reagent	products	branching ratio	k_{exp}[a] ($cm^3\ s^{-1}$ $molecule^{-1} \times 10^{10}$)	k_{calc}[b] ($cm^3\ s^{-1}$ $molecule^{-1} \times 10^{10}$)	efficiency[c]
CO_2	$HSiOS^- + CO$ extr[d]	1.0	0.34 ± 0.04	$k_L = 7.90$	0.043
COS[e]	$HSiS_2^- + CO$ extr	0.14			
	$HSiOS^- + CS$ extr	0.33	0.11 ± 0.01	$k_{var} = 13.6$	0.008
	HS^- + Si,C,O,S	0.53			
CS_2	$HCS_2^- + SiS$ H-trans	0.40	0.19 ± 0.03	$k_L = 11.9$	0.016
	$HSiS_2^- + CS$ extr	0.60			
SO_2	$HSiOS^- + SO$ extr	1.0	13.5 ± 2.0	$k_{var} = 18.0$	0.75
O_2	$HSiOS^- + O$	0.72	0.05 ± 0.01	$k_L = 6.43$	0.008
	$SiO_2S^- + H$	0.28			
C_6F_6	$FSiS^- + C_6F_5H$	0.42	3.9 ± 0.5	$k_L = 11.2$	0.35
	$HF_2SiS^- + C_6F_4$	0.58			

[a] Experimental rate coefficients are designated as k_{exp}. [b] Computed rate coefficients are given as k_L (Langevin) or k_{var} (variational). Reference to their calculation are given in ref 38. [c] The efficiency is the k_{exp}/k_{cal}. [d] Hydride transfer is abbreviated as H-trans, and four-membered ring extrusion is abbreviated as extr. [e] COS has a small H_2S impurity which affects the rate coefficients and branching ratios (see text).

Table IV. Products, Branching Ratios, Rates Coefficients, and Efficiencies of $HSiNH^-$ Reactions

reagent	products	branching ratio	k_{exp}[a] ($cm^3\ s^{-1}$ $molecule^{-1} \times 10^{10}$)	k_{calc}[b] ($cm^3\ s^{-1}$ $molecule^{-1} \times 10^{10}$)	efficiency[c]
CO_2	HCO_2^- + H,Si,N H-trans[d]	0.29			
	$NCO^- + H_2SiO$ scis	0.38	3.5 ± 0.3	$k_L = 8.52$	0.41
	$HSi(NH)O^- + CO$ extr	0.28			
	$HSiO_2^- + HCN$ extr	0.05			
COS[e]	$HSiS^- + HNCO$ scis	0.89			
	$NCO^- + H_2SiS$ scis	0.05	3.5 ± 0.3	$k_{var} = 14.9$	0.24
	$HSi(NH)S^- + CO$ extr	0.06			
CS_2	$NCS^- + H_2SiS$ scis	0.02	4.6 ± 0.4	$k_L = 13.1$	0.35
	$HSi(NH)S^- + CS$ extr	0.98			
SO_2	HSO_2^- + H,Si,N H-trans	0.18			
	$NSO^- + H_2SiO$ scis	0.09			
	$HSi(NH)O^- + SO$ extr	0.56	17.2 ± 1.7	$k_{var} = 19.7$	0.87
	$HSiO_2^-$ + H,N,S extr	0.13			
	$HSi(NH)S^-$ or $HSi(NH)O_2$	0.04			
O_2	$HSi(NH)O^- + O$	0.44			
	$HNSiO_2^- + H$	0.39	0.08 ± 0.03	$k_L = 6.84$	0.012
	$HSiO_2^- + NH$	0.17			
C_6F_6	$HSiNC_6F_5^- + HF$	1.0	9.6 ± 1.0	$k_L = 12.7$	0.75

[a] Experimental rate coefficients are designated as k_{exp}. [b] Computed rate coefficients are given as k_L (Langevin) or k_{var} (variational). References to their calculation are given in ref 38. [c] The efficiency is the k_{exp}/k_{cal}. [d] Hydride transfer is abbreviated as H-trans, four-membered ring extrusion is abbreviated as extr, and four-membered ring scission is abbreviated scis. [e] COS has a small H_2S impurity which affects the rate coefficients and branching ratios (see text).

suggested for $HSiO^-$ will be used exclusively in this paper.

Gas-Phase Anion Proton Affinity of $HSiS^-$ and $HSiNH^-$. The gas-phase anion proton affinities[22] of $HSiS^-$ and $HSiNH^-$ have been measured using bracketing techniques.[23] Although bracketing measurements to obtain acidities are inherently less accurate than other techniques,[23-26] they are necessitated here because H_2SiS and $HSiNH_2$, the most stable conjugate acid isomers,[27] are not readily available for study in the flowing afterglow. Table II presents the results of the bracketing studies.[23] Thus, $HSiS^-$ abstracts a proton from HCl, but not formic acid, leading to a bracketed $\Delta G°_{acid}$ of 333 ± 6 kcal/mol for H_2SiS. $HSiNH^-$ abstracts a proton from pyrrole, but not from CF_3CH_2OH establishing $\Delta G°_{acid} = 352 \pm 3$ kcal/mol as the acidity of $HSiNH_2$. The corresponding $\Delta G°_{acid}$ values for $SiCH_2$ and H_2SiO are 352 ± 3 and 356 ± 8 kcal/mol. Although it is difficult to comment on trends in the acidities of such compounds since so few are known, it is interesting that H_2SiS is so much more acidic than H_2SiO.

Reaction Chemistry of $HSiS^-$ and $HSiNH^-$. We have used a variety of small neutral molecules to probe the reactivity of anions.[7,9,28] Since our FA-SIFT studies give only *m/z* data on ion–molecule reactions, such neutral reactants have served as indirect characterization tools, allowing us to obtain structural information about anions. Both $HSiS^-$ and $HSiNH^-$ have been reacted with CO_2, CS_2, COS, and SO_2 as well as other more complex neutral molecules.

The general reaction patterns for silicon-containing anions at this oxidation level ($HSiO^-$, $HSiS^-$, and $HSiNH^-$) are given in Scheme I. A close variation of Scheme I was first proposed in our $HSiO^-$ studies.[7] In the more general form given here, it summarizes all of the information obtained in our studies of $HSiO^-$ with CO_2, COS, and CS_2 as well as capturing the essence of the reaction chemistry of $HSiS^-$ and $HSiNH^-$ with these neutrals. In using COS as the key small neutral reactant, Scheme I illustrates most of the important features of these species. Thus, the ion–dipole attraction of $HSiX^-$ and COS leads first to a

---

(22) Bursey, M. M. *Mass Spectrom. Rev.* **1990**, *9*, 503–540. The anion proton affinity of X^- is $-\Delta H$ for the reaction of $X^- + H^+ \rightarrow HX$; thus, the greater the numeric value of an anion proton affinity, the stronger the basic characteristics of X^-. The anion proton affinity, thus, is a measure of the acidity of HX. In this paper, acidities are expressed as $\Delta G°_{acid}$. It is important to understand that the larger the numerical value for an acidity, the less acidic it is.

(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl 1. All the acidities cited in this paper, unless otherwise indicated, come from this reference.

(24) McLuckey, S. A.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1312–17.

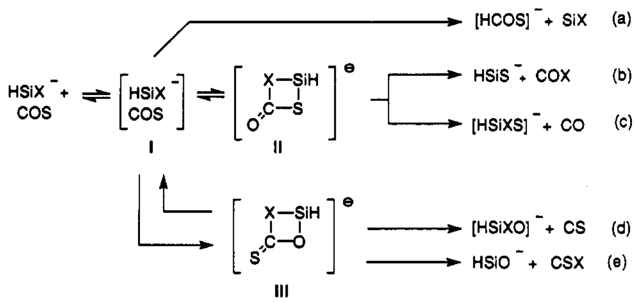
(25) Nourse, B. D.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1991**, *106*, 249–272.

(26) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517–29.

(27) We have adopted a convention in this paper for the protonated parent species of anions which might have more than one isomeric structure. These are considered to be the most stable of the isomeric species as determined by computational studies. We have done so primarily for the sake of simplicity and do not imply that protonation occurs to make the most stable isomer. Indeed, barriers to protonation may be important and computational studies are under way to examine this question (see ref 20).

(28) DePuy, C. H.; Damrauer, R. *Organometallics* **1984**, *3*, 362–5.

Scheme I



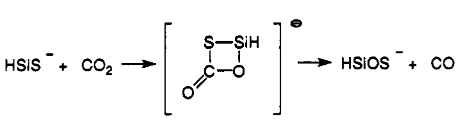
complex (I) typical of all ion–molecule reactions. Complex I can either (1) transfer a hydride to COS (path a) or (2) add to COS (paths b–d). Addition leads to the four-membered intermediates II and III. Intermediate II can react by ring scission of the four-membered ring (the equivalent of a 2 + 2 cycloreversion) leading to $HSiS^-$ and COX (path b) or by ring extrusion leading to $[HSiXS]^-$ and CO (path c). Intermediate III can undergo ring extrusion by path d, although this is a minor process for $HSiO^-$. Ring scission from III has been observed with $HSi^{18}O^-$ and is included as path e in the scheme.

Isotope labeling studies of $HSiO^-$ reacting with CO_2 using ^{18}O-labeled $HSiO^-$ have established the intermediacy of four-membered species like II and III in these reactions. In addition, they have demonstrated that ion–dipole complex formation and four-membered ring formation is reversible for $HSiO^-$.[7] Schmidt and Gordon, in their computational studies of the reactions of $SiCH^-$ with CO_2, COS, CS_2, and SO_2, have reported that stable four-membered ring intermediates are minima on the potential surface of these reactions.[10]

Reactions of $HSiS^-$ and $HSiNH^-$ with Representative Neutral Compounds. A summary of the reaction products, rate coefficients, efficiencies, and branching ratios for representative neutral reagents is given in Table III for $HSiS^-$ and in Table IV for $HSiNH^-$. The structures of the reaction products in these tables are deduced from their *m/z* and by analogy with previous studies.

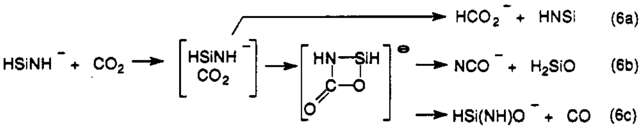
Scheme I gives a consistent picture of the reactivity of $HSiS^-$ and $HSiNH^-$ with CO_2, COS, and CS_2. In the following sections, many of these reactions, as well as those with more complex neutral reactants, will be considered in greater detail. In addition, the kinetic studies will be discussed in terms of the nature of the different reactivity patterns these anions display.

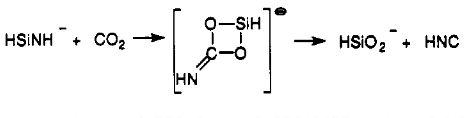
A. Reactions of $HSiS^-$ and $HSiNH^-$ with CO_2. In contrast to $HSiO^-$ which reacts with CO_2 by both hydride transfer (45%) and ring extrusion (55%) pathways,[7] $HSiS^-$ gives only the ring extrusion reaction (eq 5) [Scheme I(c)]. The absence of hydride transfer indicates, as we suggested earlier,[7] that the hydride affinity of SiS is greater than that of CO_2, which is 52 kcal/mol,[29,30] and of SiO, which is 49 ± 5 kcal/mol.[7]



(5)

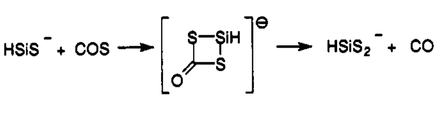
The reaction of $HSiNH^-$ and CO_2 leads to four products (eq 6 and 7). Hydride transfer gives HCO_2^- (29%) from complex I (eq 6a) [Scheme I(a)]. The structure of the neutral product in eq 6a follows from an experiment in which $HSiND^-$ and CO_2 give only HCO_2^-. This hydride transfer reaction indicates that HNSi[3,15,32] has a smaller hydride affinity than that of CO_2 (52 kcal/mol). In addition, the intermediate four-membered ring yields NCO^- by ring scission, followed by proton transfer (38%) (eq 6b) [Scheme I(b)] and $HSi(NH)O^-$ by ring extrusion (28%) (eq 6c) [Scheme I(c)]. A small amount of $HSiO_2^-$ also forms, presumably when the first formed four-membered intermediate in eq 6 opens and recloses to a different four-membered ring intermediate that extrudes HNC (5%) (eq 7).



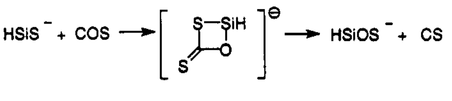


(7)

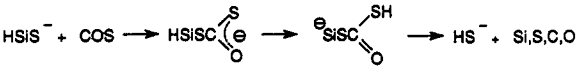
B. Reactions of $HSiS^-$ and $HSiNH^-$ with COS. Hydride transfer [Scheme I(a)] to COS (hydride affinity = 67 kcal/mol)[29,30] can be shown to occur using $HSi^{34}S^-$. The labeling experiment is required because both $HSi^{32}S^-$ and $HCO^{32}S^-$ have the same mass. Path b of Scheme I does not operate in the $HSiS^-$ reaction although eq 8 and 9 illustrate the importance of paths c and d. The corresponding $HSiO^-$ reaction gave 20% hydride transfer [Scheme I(a)], 65% ring scission [Scheme I(b)], and 15% ring extrusion [Scheme I(c)]. A third open product channel for $HSiS^-$, giving HS^-, may operate as well (eq 10). Unfortunately, the rate coefficients and branching ratios for these reactions are made uncertain by a small H_2S impurity in the COS. Thus, the product of eq 8 ($HSiS_2^-$) also results in the reaction of $HSiS^-$ and H_2S. The rate coefficient for this latter process is ≈3×10^{-10} cm^3 s^{-1} molecule^{-1} (one measurement only).



(8)

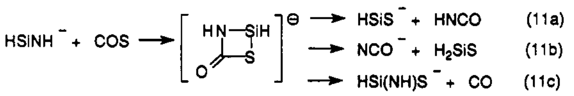


(9)

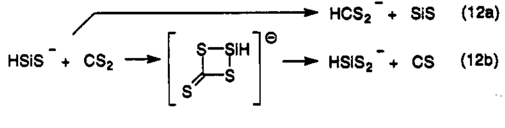


(10)

$HSiNH^-$ gives three products with COS (eq 11). Two of these arise from ring scission which initially leads to $HSiS^-$ (eq 11a). Proton transfer to HNCO gives a small amount of NCO^- as well (eq 11b) [(11b) is not really a separate channel, but displayed this way for clarity]. Ring extrusion gives $HSi(NH)S^-$ (6%) (eq 11c) [Scheme I(c)]. Ring extrusion by Scheme I(d) was not observed. No hydride-transfer reaction product could be detected because the *m/z* of $HCOS^-$ is the same as $HSiS^-$. The branching ratios and rate coefficients in eq 11 are not affected by the H_2S impurity in COS. Thus, of the observed reaction products of $HSiNH^-$ and H_2S, namely, HS^- (major) and $HSi(NH)S^-$ (minor), only $HSi(NH)S^-$ is observed in reaction 11.



C. Reactions of $HSiS^-$ and $HSiNH^-$ with CS_2. Both hydride transfer (40%) (eq 12a) (path a) and ring extrusion pathways (60%) (eq 12b) are observed for $HSiS^-$ reacting with CS_2 (eq 12).



---

(29) Bartmess, J. E. *Mass Spectrom. Rev.* **1989**, *8*, 297–343.

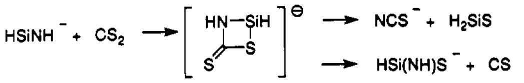
(30) Squires, R. R. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; p 373.

(31) The convention referenced in footnote 27 also applies to neutral products in reactions we have studied. Thus, if a computational study suggests that one isomeric neutral is more stable than another, and, if that isomer is a logical product in terms of its connectivity, then that structure is given. In the case referenced here, hydride transfer to CO_2 could logically give either of two [H,Si,N] isomers, but HNSi is by far more stable than HSiN.

(32) Personal communication: Travers, M. J.; Ellison, G. B., 1990. This extensive electron affinity compilation is unpublished and is available on request from R.D.

Such a reactivity pattern is very similar to that of $HSiO^-$.[7]

$HSiNH^-$ reacts with CS_2 to give a small amount of ring scission (2%) (eq 13a) and an ion with $m/z = 76$ (98%) which could be

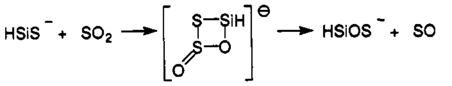


(13a)

(13b)

either the hydride-transfer product, HCS_2^-, or a ring-extrusion product, $HSi(NH)S^-$. Studies using $C^{34}S_2$, showing that only one sulfur is incorporated in the product ion, establish the identity of the 98% channel anion as $HSi(NH)S^-$ (eq 13b).

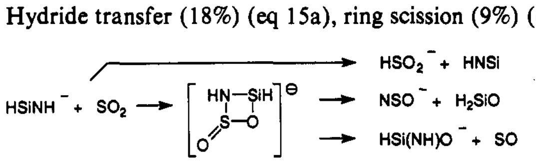
D. Reactions of HSiS⁻ and HSiNH⁻ with SO₂. $HSiS^-$ reacts with SO_2 to give only a ring extrusion product $HSiOS^-$ (eq 14).



(14)

The corresponding reaction with $HSiO^-$ gave a significant amount of electron transfer (20%), a trace of hydride transfer, and ring extrusion (80%).[7] The failure of $HSiS^-$ to transfer an electron to SO_2 indicates that the electron affinity of the HSiS radical is greater than 1.1 eV.[32]

Hydride transfer (18%) (eq 15a), ring scission (9%) (eq 15b),

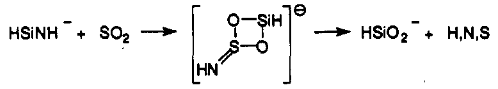


(15a)

(15b)

(15c)

and ring extrusion (56%) (eq 15c) are all characteristic reaction pathways for $HSiNH^-$. In addition, 13% of $HSiO_2^-$ is observed which apparently arises in an extrusion reaction of the four-membered intermediate shown in eq 16. Finally, an anion with

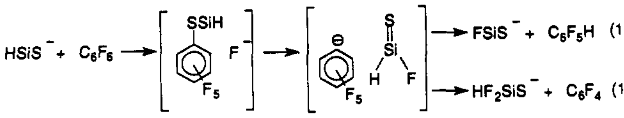


(16)

$m/z = 76$, which is likely $HSi(NH)S^-$, is detected in small amounts (4%).

E. Reactions of HSiS⁻ and HSiNH⁻ with O₂. The reactions of $HSiS^-$ and $HSiNH^-$ with O_2 are similar to those obtained with $HSiO^-$,[7] although a detailed accounting of the formation of products is difficult (see Tables III and IV).

F. Reactions of HSiS⁻ and HSiNH⁻ with C₆F₆. Hexafluorobenzene has been shown to have unusual reactivity with anions.[2,7,9] Reaction with $HSiS^-$ gives two product channels in contrast to the three product channels observed for $HSiO^-$. Nucleophilic attack of $HSiS^-$ initially gives a Meisenheimer adduct (not shown) from which F^- detaches, giving the reaction complex shown in eq 17. Attack of F^- in this complex leads to a complex of $C_6F_5^-$

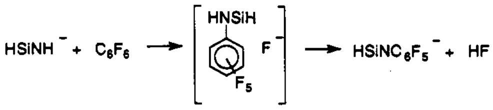


(17a)

(17b)

and H(F)Si=S from which the products arise. In one case, $C_6F_5^-$ abstracts a proton from H(F)Si=S (eq 17a); in the other, F^- loss from $C_6F_5^-$ and addition to H(F)Si=S occurs (eq 17b). A similar explanation was used to describe the products in the $HSiO^-$ reaction; however, in that case a dissociation channel from the final complex leading to $C_6F_5^-$ was also observed.[7]

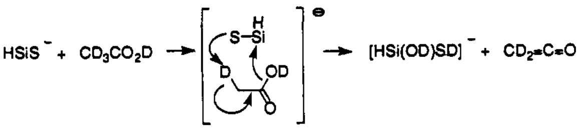
The reaction of $HSiNH^-$ and C_6F_5 takes a simpler course since the intermediate from which F^- has detached has an acidic proton that is abstracted by F^- (eq 18). Presumably, the N–H acidity



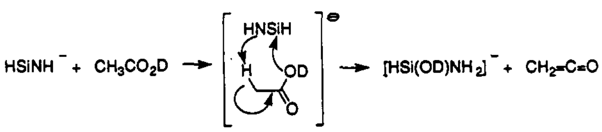
(18)

displayed here is the result of activation by both silicon and the adjacent pentafluorobenzene moiety.

G. Reactions of HSiS⁻ and HSiNH⁻ with Acetic Acid. Both $HSiS^-$ and $HSiNH^-$ undergo interesting reactions with acetic acid and its deuterated derivatives. Such reactions establish that α-hydrogens or deuteria and O–H or O–D are transferred to these anions, possibly in a cyclic manner. The essential features of this reaction channel are illustrated in eq 19 and 20, assuming a cyclic



(19)



(20)

pathway for simplicity. The acidity of H_2SiS ($\Delta G°_{acid} = 333$ kcal/mol) suggests that no proton abstraction channel between acetic acid and $HSiS^-$ should operate as is observed (see Table II). On the other hand, $HSiNH^-$ with a corresponding $\Delta G°_{acid} = 352$ kcal/mol does abstract a proton from acetic acid ($\Delta G°_{acid} = 342$ kcal/mol)[23] as an independent process.

H. Reactions of HSiS⁻ and HSiNH⁻ with Alcohols. The anion $HSiS^-$ undergoes no deuterium exchange with CH_3CH_2OD or CF_2HCH_2OD even though reactions with deuterated alcohols expose both exchange and redox channels in the reactions of $HSiNH^-$ (eqs 21–25). Equations 21, 22a, and 23a demonstrate

$$HSiNH^- + CD_3OD \longrightarrow HSiND^- + CD_3OH \quad (21)$$

$$HSiNH^- + CH_3CH_2OD \longrightarrow HSiND^- + CH_3CH_2OH \quad (22a)$$

$$ \longrightarrow H_2(NHD)Si^- + CH_3CHO \quad (22b)$$

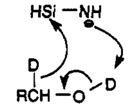
$$HSiNH^- + CD_3CD_2OD \longrightarrow HSiND^- + CD_3CD_2OH \quad (23a)$$

$$ \longrightarrow HD(NHD)Si^- + CD_3CDO \quad (23b)$$

$$HSiNH^- + CH_3CD_2OH \longrightarrow HD(NH_2)Si^- + CH_3CDO \quad (24)$$

$$HSiNH^- + CD_3CH_2OH \longrightarrow H_2(NH_2)Si^- + CD_3CHO \quad (25)$$

the hydrogen–deuterium exchange. The redox channel, illustrated by eq 22b, 23b, 24, and 25, requires a β-hydrogen and may occur as illustrated through a cyclic, six-membered transition state (IV).



IV

If such a mechanism holds, we would expect that an alcohol having no β-hydrogen would not react through the redox channel. Indeed, *tert*-butyl alcohol does not react with $HSiNH^-$.

Hydride Affinities and Thermochemistry. In our earlier studies, we determined the hydride affinity (HA) of SiO (49 ± 5 kcal/mol), the heat of formation of $HSiO^-$ (−38 ± 5 kcal/mol), and the heat of formation of H_2SiO (−36 ± 10 kcal/mol).[7] Since the heat of formation of SiS is known and since we have determined the acidity for H_2SiS, an estimation of the heats of formation of $HSiS^-$ and H_2SiS rests on a determination of the HA of SiS. Hydride-transfer reactions to CS_2 (HA = 67 kcal/mol) and COS (HA of 67 kcal/mol) occur while reaction with SO_2 (HA = 63 kcal/mol) does not.[29,30] We assign a tentative value of the HA for SiS as 65 ± 5 kcal/mol although we have some doubts about such HA determinations.[33] A recent computational study by

---

(33) We are uncertain about the possibility of barriers in hydride affinity measurements and are undertaking computational studies to probe this (see ref 20). In addition, as a referee has pointed out, the hydride transfer channels used for the bracketing determination are not highly efficient.

Bruna and Grein has estimated the HA of SiS at the MP4 level to be 56.7 kcal/mol.[34] Using our tentative HA value, the heat of formation of SiS of 25.3 kcal/mol (at 298.15 K),[35] and ΔH°_{acid} = 339 kcal/mol for H_2SiS, an estimated heat of formation for $HSiS^-$ and H_2SiS can be obtained.[36]

A similar analysis of $HSiNH^-$ cannot be carried out since experimental heats of formation of H,Si,N species are unknown (although a recent estimate of the heat of formation of HNSi has been reported).[37] In addition, the hydride-transfer reactions of $HSiNH^-$ exhibit inconsistent behavior since transfer occurs to CH_3NCO, SO_2, and CO_2 (HA's = 73, 63, and 52 kcal/mol), but not to CS_2, CF_3COCH_3, or O_2 (HA's = 67, 59, and 58 kcal/mol).[33]

By combining the heats of formation of $HSiS^-$ and $HSiO^-$ with those of COS and CO_2, we can estimate the heat of reaction of $HSiO^- + COS \rightarrow HSiS^- + CO_2$ as −25 kcal/mol. We have observed this reaction earlier.[7] The reverse reaction, which $HSiS^-$ does not undergo, is clearly not favored thermochemically.

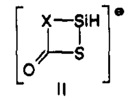
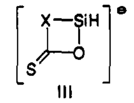
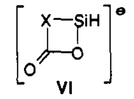
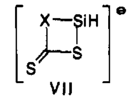
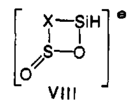
Kinetics and Reactivity Comparisons. Rate coefficients and efficiencies for the reactions of $HSiS^-$ and $HSiNH^-$ are presented in Tables III and IV. They follow generally similar trends even though the magnitudes of the rate coefficients and efficiencies are different. Thus, $HSiS^-$ reacts with CO_2, COS, and CS_2 with roughly the same rate coefficient and efficiency, but these rate coefficients and efficiencies are at least an order of magnitude smaller than for the corresponding reactions of $HSiNH^-$ and are near the lower limit of measurement. Interestingly, the rate coefficients and efficiencies for $HSiO^-$ reacting with CO_2, COS, and CS_2 are quite similar[7] to those of $HSiNH^-$. On the other hand, the reactions of $HSiS^-$, $HSiNH^-$, and $HSiO^-$ with SO_2 and C_6F_6 are much faster, proceeding with efficiencies of 0.75, 0.87, and 1.21 for the SO_2 reaction and of 0.35, 0.75, and 0.63 for the C_6F_6 reaction.[7] Given these results, it is surprising that $HSiS^-$ and $HSiNH^-$ react with O_2 with efficiencies of 0.008 and 0.012 when our reported efficiency for $HSiO^-$ with O_2 was 0.66. In checking this, we have found that a typographical error was introduced in our original report.[7] The correct value for the rate coefficient is 0.45×10^{-10} cm^3 molecule^{-1} s^{-1} (with a corresponding efficiency of 0.066). These are consistent with the results reported therein.

While it is especially evident that $HSiS^-$ is less reactive than $HSiNH^-$ with the less reactive neutral reagents like CO_2, COS, and CS_2, it is also the case with SO_2 and C_6F_6. Even in their very slow reactions with O_2, both $HSiS^-$ and $HSiNH^-$ show this order of reactivity. It is also clear that $HSiS^-$ reacts much more slowly than $HSiO^-$. We suggest that the similarity in reactivity between $HSiNH^-$ and $HSiO^-$ is largely a reflection of the base strengths of these anions. Thus, $HSiNH^-$ and $HSiO^-$, whose conjugate acids have similar acidities, are more reactive than the less basic $HSiS^-$.

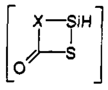
The mechanisms of many of these reactions have been discussed earlier, particularly for CO_2, COS, CS_2, and SO_2 in terms of Scheme I. The similarity of the reaction products of $HSiS^-$, $HSiNH^-$, and $HSiO^-$ is compelling evidence that their reaction mechanisms are closely related. The trends in the kinetic studies just discussed suggest this as well.

Questions related to the formation and fate of the four-membered ring intermediates in these reactions are an important aspect of the reaction mechanisms, but were not considered in detail for $HSiO^-$. To address these, we will first consider the two possible four-membered intermediates formed in the COS reactions, after which we will discuss the decomposition of these intermediates to ring-scission and ring-extrusion products. The COS reactions are particularly informative since two distinct four-membered intermediates (II and III) can form for each anionic reactant.

Table V. Relative Partitioning Yields for Reactions with Four-Membered Ring Intermediates

four-membered ring ntermediate	reactant	X	rel yield[a] of ring scission product (%)	rel yield[a] of ring-extrusion product (%)
 II	COS	X = O	81	19
		X = S		30[b]
		X = NH	94	6
 III	COS	X = O		trace
		X = S		70
		X = NH		
 VI	CO_2	X = O		100
		X = S		100
		X = NH	58	42
 VII	CS_2	X = O		100
		X = S		100
		X = NH	2	98
 VIII	SO_2	X = O		100
		X = S		100
		X = NH	14	86

[a] The relative yields have been calculated by considering only the scission and extrusion channels and taking the percentages of these. [b] The yield of this product is affected by the small impurity of H_2S in COS.


II

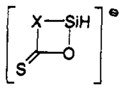
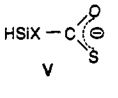

III

Table V presents data on the distribution of products derived from these two intermediates for X = O, S, and NH as well as information on the relative amounts of II and III formed. Table V presents the relative yields of only those products which derive from such intermediates. Intermediate II is strongly favored for both X = O and NH, while both II (30%) and III (70%) are formed when X = S. These results suggest that the more electronegative O and N atoms adjacent to silicon in $HSiO^-$ and $HSiNH^-$ make silicon more susceptible to interaction with sulfur than oxygen. With X = S this effect is attenuated and a greater amount of III than II forms. In essence, this argues that the ambident ion, V, which closes to either II or III, is strongly influenced by the nature of the X group.


V

Once a particular four-membered ring intermediate is formed, is there a pattern to its decomposition? The COS products reveal that the X = S intermediate tends to decompose one way, and the X = NH and X = O intermediates decompose another way. Thus, II gives only ring extrusion for X = S, but for X = NH and O, ring scission dominates ring extrusion by factors greater than 4. In III, which only forms in significant amounts when X = S, ring extrusion is exclusive. Aside from the COS reactions, we see from Table V that ring scission products only occur when X = NH. At least 86% ring extrusion occurs for X = S, NH, and O in the CS_2 and SO_2 reactions, but for the X = NH anion with CO_2 a larger amount of ring scission is observed. We see from VI and VII, when X = NH in the CO_2 and CS_2 reactions, that scission dominates only when HNCO forms, but not when the X-containing component contains sulfur. These results suggest

---

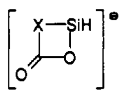
(34) Bruna, P. J.; Grein, F. *J. Phys. Chem.* **1992**, *96*, 6617–6623.

(35) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl 1.

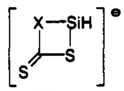
(36) The heats of formation of $HSiS^-$ and H_2SiS are crudely estimated to be −5 and 22 kcal/mol, respectively. The data used in these calculations come from refs 23 and 34. They are 25.3 kcal/mol for SiS, 34.7 kcal/mol for H^-, and 365.7 kcal/mol for H^+.

(37) Wlodek, S.; Rodriquez, C. F.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Chem. Phys. Lett.* **1988**, *143*, 385–389.

(38) Chesnavich, W. J.; Su, T.; Bowers, M. T. *J. Chem. Phys.* **1980**, *72*, 2641.



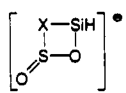
VI



VII

that the X-containing scission product controls partitioning. This is particularly clear for the reaction of CO_2 with $HSiS^-$ and $HSiNH^-$. In both of these cases the Si-containing ring-scission product would be $HSiO^-$, but only X = NH gives any ring-scission product (see VI). Since the X = NH and O anions have similar reactivity, we might expect that intermediate VI with X = O would also undergo ring scission. It is likely that it does, but this decomposition is nothing more than a reversal of the formation of VI.

The partitioning of products from a particular four-membered ring intermediate cannot be assessed using thermochemistry since the requisite heats of formation are unknown. Nevertheless, in looking at the reactions we have studied, it seems reasonable that thermochemical factors are dominant. Thus, in almost every case ring extrusions dominate because $HSiXO^-$ or $HSiXS^-$ and CO, CS, or SO products are favored over the corresponding XCO, XCS, or XSO and $HSiO^-$ or $HSiS^-$. In the two examples in which ring scission occurs in greater the 10% relative yield, HNCO/$HSiO^-$ and HNSO/$HSiO^-$ (see VIII) form. Although we presume that these channels are thermochemically competitive with the ring extrusion ones, we cannot rule out dominant kinetic effects.



VIII

Conclusions

We have examined the detailed reactions of $HSiS^-$ and $HSiNH^-$ with a variety of neutral reagents. While their reaction chemistry is very similar and best explained using a model which was first developed for $HSiO^-$, their reactivities differ significantly. Thus, $HSiNH^-$ and $HSiO^-$ have similar reactivities and are much more reactive than $HSiS^-$. Computational studies of both $HSiS^-$ and $HSiNH^-$ have also been carried out.

Acknowledgment. R.D. wishes to thank the National Science Foundation (CHE-8921522) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. R.A.J.O'H wishes to thank the National Science Foundation (CHE-9122828) for support.

An Empirical Method To Calculate Average Molecular Polarizabilities from the Dependence of Effective Atomic Polarizabilities on Net Atomic Charge

Kyoung Tai No,[*,†,‡] Kwang Hwi Cho,[‡] Mu Shik Jhon,[†,§] and Harold A. Scheraga[*,⊥]

Contribution from the Department of Chemistry, Soong Sil University, Sang Do 5 Dong 1-1, Dong Jak Gu, Seoul 156-743, Korea, Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-gu, Taejon 305-701, Korea, and Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853-1301.

Received July 22, 1992

Abstract: An empirical method for the calculation of average molecular polarizability is introduced. In this method, the effective atomic polarizabilities are described as a function of net atomic charges which are obtained with the modified partial equalization of orbital electronegativity (M-PEOE) method. The effective atomic polarizability is derived with the aid of the Thomas–Fermi model of multiply-charged spherical ions. The calculated polarizabilities agree well with experimental data. Nonbonded potential parameters are also calculated as a function of net atomic charges from the effective atomic polarizabilities.

Introduction

It is useful to calculate the polarizabilities of parts of molecules, *fractional polarizabilities*, based on the *additivity hypothesis*. This hypothesis has been tested by several workers.[1-8] The parts of a molecule are usually the bonds[5-7] or the functional groups in the molecules.[4,8] According to the extensive studies mentioned above, the molecular polarizability can be written as a sum of atomic polarizabilities. However, the environment of the atoms in a molecule must be considered in the parametrization of the polarizability. The additivity hypothesis works well if hybrid atomic, group or bond parameters are used in the analysis instead of atomic polarizability. These fractionally-decomposed polarizabilities can be used for the calculation of molecular polarizabilities and other molecular properties such as molar refraction[3,4] that can be regarded as additive sums of their individual contributions. Applequist et al.[7c] introduced an interaction model instead of the additivity model. In their work, the suitability of an isotropic atom model for predicting anisotropy of polyatomic molecules was considered. The computed average polarizabilities agreed well with experimental data (with an error of between 1 and 5%), and the discrepancies between theory and experiment for the principal components of the polarizability were often of the order of 10%.

[†] Member of the Center for Molecular Science, Korea.
[*] To whom correspondence should be addressed.
[‡] Soong Sil University.
[§] Korea Advanced Institute of Science and Technology.
[⊥] Cornell University.

(1) Silberstein, L. *Philos. Mag.* **1917**, *33*, 92.
(2) Pitzer, K. S. *Adv. Chem. Phys.* **1959**, *2*, 59.
(3) (a) Eisenlohr, F. *Z. Phys. Chem.* (*Leipzig*) **1911**, *75*, 585. (b) Eisenlohr, F. *Z. Phys. Chem.* (*Leipzig*) **1912**, *79*, 129.
(4) (a) Vogel, A. I. *J. Chem. Soc.* **1948**, 1833. (b) Vogel, A.; Cresswell, W. T.; Jeffery, G. J.; Leicester, J. *Chem. Ind.* **1950**, 358.
(5) von Steiger, A. L. *Berichte* **1921**, *54B*, 1381.
(6) Smyth, C. P. *Philos. Mag.* **1925**, *50*, 361.
(7) (a) Denbigh, K. G. *Trans. Faraday Soc.* **1940**, *36*, 936. (b) Vickery, B. C.; Denbigh, K. G. *Trans. Faraday Soc.* **1949**, *45*, 61. (c) Applequist, J.; Carl, J. R.; Fung, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2952.
(8) (a) Haverkort, J. E. M.; Baas, F.; Beenakker, J. J. M. *Chem. Phys.* **1983**, *79*, 105. (b) Waite, J.; Papadopoulos, M. G. *J. Chem. Phys.* **1985**, *83*, 4047.

0002-7863/93/1515-2005$04.00/0 © 1993 American Chemical Society