magnetic sector (Magnet II).[11] MI and CAD spectra were obtained as ion-kinetic-energy scans of MS-I selected ions decomposing in the 3rd field-free region (between MS-I and ESA II) or as mass scans of ions decomposing in the 4th field-free region (between ESA II and Magnet II). The reported spectra are averages of 15–100 repetitive scans.

Compounds **1**, **1a**, and **1b** were prepared by benzylation[35] (benzyl bromide, 1.2 eq, silver oxide, 2.5 eq, dimethyl formamide, 20 °C, 8 h) of ethanol, ethanol-*1,1*-d_2, and ethanol-*1,1,2,2,2*-d_5, respectively. To prepare **1c**, benzoic-d_5 acid (Aldrich) was reduced to benzyl-*2,3,4,5,6*-d_5 alcohol which was ethylated[35] with ethyl iodide. Ethers **1** and **1a–1c** were purified by vacuum distillation and their mass spectra revealed no impurities.

3-Methyl-2,4-dioxaspiro[5.5]undeca-8,10-diene. To a stirred solution of 3-methyl-2,4-dioxaspiro[5.5]undec-8-ene[36] (1.68 g, 10 mmol, mixture of diastereoisomers) in dichloromethane (30 mL) at −50 °C was added a solution of bromine (1.65 g, 10.3 mmol) in dichloromethane (20 mL). After 15 min the solvent was evaporated in vacuo to give a light yellow oil that solidified upon standing at 0 °C overnight. The dibromo derivative (3.2 g) was dissolved in dimethyl formamide (8 mL) and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene[37] (6 g) at 140 °C under argon for 6 h. The cooled mixture was diluted with water (30 mL) and pentane (30 mL), the water layer was extracted twice with pentane (10 mL), the pentane layers were washed with ice-cold 5% HCl (2 × 100 mL) and water and dried with potassium carbonate, and pentane was distilled off through a 20 cm Vigreaux column. The residue was distilled (short path, 100 °C/10 Torr) to yield 825 mg (50%) of product as a mixture of diastereoisomers. MS (*m/z*, rel intensity): 166 ($M^{\cdot+}$, 1.1), 136 (0.2), 122 (1), 105 (5.3), 92 (100), 91 (81), 90 (16), 79 (4), 77 (7), 73 (2.5), 65 (14), 52 (4), 51 (9), 43 (15), 39 (19). ^{1}H NMR ($CDCl_3$, 200 MHz): 1.32 d, 1.34 d (CH_3), 1.84 m (CH_2), 2.62 m (CH_2), 3.40, 3.44 ddd (*J* = 11.0, 1.2, 1.1 Hz, CH_2O), 3.90, 3.98 dd (*J* = 11.0, 1.2 Hz, CH_2O), 4.62, 5.10 m (OCHO), 5.60, 5.80, 6.00, 6.22 m (CH=).

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Gas-Phase Chemistry of the Silaformyl Anion, $HSiO^-$

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Abstract: The silaformyl anion, $HSiO^-$, has been prepared by collisionally induced dissociation (CID) of H_3SiO^- in a tandem flowing afterglow selected ion flow tube (FA-SIFT). The chemistry of the silaformyl anion has been studied in detail. Reactions with CO_2, COS, CS_2, SO_2, O_2, acetic acid, nitromethane, and hexafluorobenzene reveal a rich chemistry. For example, the silaformyl anion reacts with CO_2 by both an oxidative pathway giving $HSiO_2^-$ and CO and a reductive path giving SiO and HCO_2^-. Typically, the silaformyl anion, which could have several sites of reactivity, behaves both as an oxygen nucleophile and as a hydride donor. Detailed mechanistic studies have been carried out on many of these reactions with isotopically labeled $H^{29}SiO^-$ and $HSi^{18}O^-$. In addition to its reaction chemistry, the heat of formation of the silaformyl anion, its basicity, and the heat of formation of its parent compound have been estimated. Ab initio computations on the silaformyl anion have been carried out and demonstrate that $HSiO^-$ is more than 40 kcal/mol more stable than $HOSi^-$.

Silicon analogues of alkanes and cycloalkanes, including those of some highly strained molecules, are generally stable compounds whose chemistry can readily be investigated.[1] Silicon analogues of unsaturated organic compounds, on the other hand, are with few exceptions highly reactive transient species that dimerize or polymerize readily and react rapidly with polar solvents or other components of their environment.[2] Despite the difficulties involved, a number of workers have made important contributions to our understanding of the chemistry of, for example, the silicon–carbon and silicon–oxygen double bond by examining gas-phase reactions of silenes (Si=C) and silanones (Si=O), by studying such species in matrices at low temperature, and by preparing highly substituted derivatives in which normal chemical reactions are inhibited by steric or electronic interactions.[3] Nevertheless, it is no exaggeration to say that our understanding of the chemistry of such species is extremely limited.

Our approach to this problem involves the study of the reactions of organosilicon anions in the gas phase using the flowing afterglow apparatus. This approach has a number of advantages. In the first place, we can easily prepare a large number of silicon-containing anions, ions that would likely be too reactive to study in solution.[4-8] Thus we can examine the chemical reactions of simple

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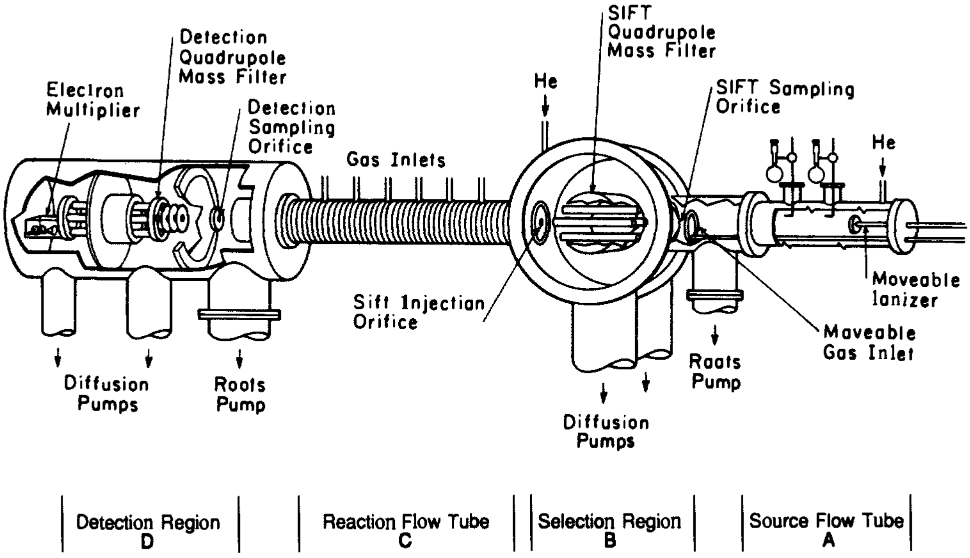

Figure 1. Schematic diagram of FA-SIFT.

systems without having to resort to the leveling effects of multiple substitutions by bulky or conjugating groups. Second, we can examine the reactions of such species with a wide variety of simple neutral reactants under single-encounter conditions so that we can determine the exact stoichiometry of the reactions. In addition, we can easily determine reaction rates, detect minor reaction pathways, and, in favorable cases, determine such fundamental thermodynamic properties as the heats of formation of the ion and related neutrals, the electron affinity of the corresponding radical, and the gas-phase acidity of the conjugate acid. We can also use the extraordinary sensitivity of our instrument to probe reaction mechanisms using ions isotopically labeled (e.g. with silicon-29) without the expense and difficulty of the laboratory synthesis of labeled precursors.

The main drawback to the method arises from the perception many chemists have that gas-phase ion–molecule reactions bear little or no relationship to reactions in solution, so that any information we might learn in our studies about how ions react in the gas phase will be of little practical use to chemists who might wish to carry out the same reactions on a reasonably sized sample in solution. We believe such perceptions to be largely false. Once a few simple energetic differences between reactions in the two phases are taken into account, similarities between reactions in the gas phase and in solution vastly outnumber their differences. It is true, of course, that a heavily solvated ion like hydroxide in aqueous or alcoholic solution differs profoundly in its chemistry from that same ion in the gas phase. But the majority of synthetically useful organic reactions of anions are carried out in aprotic solvents, where solvation effects are minimal, and we have found a remarkable parallelism, both qualitatively and quantitatively, between reactions in the two phases. We therefore believe that the general kinds of reactions we observe for these new ions in the gas phase will in general reflect the kinds of reactions that would be observed in solution.

Our object in this paper is to describe the gas-phase ion chemistry of the silaformyl anion and to make some comparisons of its properties with those of the formyl anion. From these studies we also gain some insight into its conjugate acid and its oxidation product, the silaformate ion. We also describe a method of generating unusual ions in our tandem flowing afterglow selected ion flow tube (FA-SIFT) which we feel will be useful for generating and studying a host of other highly unsaturated and reactive ions.

Experimental Section

All experiments were carried out at room temperature in our FA-SIFT. Although this instrument has been described in detail previously,[9] we believe a brief summary of its operation in these experiments is appropriate for readers who are not familiar with the technique. The FA-SIFT is shown in Figure 1. It 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) oxide ions (O^-) are prepared by electron impact on small amounts of N_2O (0.01 Torr) entrained in a rapidly flowing (40 m/s) helium stream (0.4 Torr). These ions are rapidly converted to hydroxide ions by hydrogen atom abstraction from 0.02 Torr of methane also entrained in the helium. Downstream phenylsilane is added through a moveable inlet and a rapid reaction ensues, producing a variety of ionic products (eq 1).

$$C_6H_5SiH_3 + HO^- \longrightarrow \underset{\mathrm{I}}{SiH_3O^-} + C_6H_6 \qquad (1a)$$

$$\longrightarrow C_6H_5SiH_2O^- + H_2 \qquad (1b)$$

$$\longrightarrow C_6H_5SiH_2^- + H_2O \qquad (1c)$$

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 focussed onto a quadrupole mass filter by a series of electrostatic lenses. This SIFT quadrupole is tuned to m/z 47 and the silamethoxide ion (I) is injected into the second flow tube (C) where it is again entrained in helium (0.5 Torr). At the end of the second flow tube this ion is sampled through a 0.5-mm orifice and detected by an electron multiplier. The resulting spectrum demonstrates that m/z 47 has been cleanly selected. We have previously reported some of the chemistry of this simple ion.[10]

In order 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. This potential imparts kinetic energy to the ions, but the ions are relaxed by multiple collisions with the helium buffer gas. If this potential is made sufficiently high, ions can be induced to undergo collisionally induced dissociation (CID) to form new ions.[11] For example, if the injection potential is raised to

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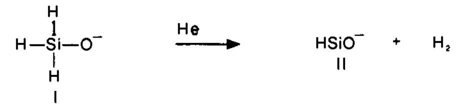
Table I. Rates and Branching Ratios for the Reactions of $HSiO^-$

reagent	products	BR[a]	k_{exp}[b]	k_c[c]	eff[d]
CO_2	$HCO_2^- + SiO$	0.45	3.2 ± 0.1	8.5	0.38
	$HSiO_2^- + CO$	0.55			
COS	$HCOS^- + SiO$	0.20	2.4 ± 0.2	12.1	0.20
	$HSiS^- + CO_2$	0.65			
	$HSiO_2^- + CS$	trace			
	$HSiOS^- + CO$	0.15			
CS_2	$HCS_2^- + SiO$	0.70	7.2 ± 0.1	13.1	0.55
	$HSiOS^- + CS$	0.30			
SO_2	$HSO_2^- + SiO$	trace	18 ± 1	14.9	1.21
	$SO_2^- + HSiO$	0.20			
	$HSiO_2^- + SO$	0.80			
O_2	$SiO_2^- + OH$	0.10	4.5 ± 0.2	6.8	0.66
	$HSiO_2^- + O$	0.50			
	$SiO_3^- + H$	0.40			
CH_3CO_2H	$HSiO_2^- + CH_3C(O)H$	0.50			
	$CH_3CO_2^- + H_2SiO$	0.50			
CH_3NO_2	$HSiO_2^- + CH_3NO$	0.70	4.2 ± 0.1[e]	27.3	0.15
	$HSiO_3^- + CH_3N$	0.15			
	$CH_2NO_2^- + H_2SiO$	0.15			
C_6F_6	$FSiO^- + C_6F_5H$	0.25	7.9 ± 0.5	12.6	0.63
	$HF_2SiO^- + C_6F_4$	0.50			
	$C_6F_5^- + HFSiO$	0.25			

[a] Branching ratio ±5%. [b] Experimental rate constant in $cm^3\ s^{-1}$ molecule^{-1} × 10^{10}. [c] Collision rate in $cm^3\ s^{-1}$ molecule^{-1} × 10^{10} as calculated by the ADO method of Su and Bowers (ref 14). [d] Efficiency defined as k_{exp}/k_{ado}. [e] Rate with CD_3NO_2 is $3.9 \pm 0.1 \times 10^{-10}\ cm^3\ s^{-1}$ molecule^{-1}.

50 V,[12] the m/z 47 ions are almost completely transformed into ions of m/z 45. We formulate this reaction as loss of H_2 (or conceivably two H atoms) from I to form the silaformyl anion (II) as shown in eq 2. The



$$\underset{\text{I}}{\mathrm{H{-}\overset{H}{\underset{H}{Si}}{-}O^-}} \xrightarrow{\text{He}} \underset{\text{II}}{\mathrm{HSiO^-}} + \mathrm{H_2} \qquad (2)$$

resulting ions subsequently undergo multiple collisions with helium and are cooled to room temperature before being allowed to react with neutral reagents. To test for the possibility of incomplete relaxation of the ions by the helium we added other, more effective quenching gases (cyclohexane, methane, argon) immediately downstream of the injection orifice and found no differences in the reactivity of the silaformyl anion. We therefore believe we are studying the chemistry of the ions under conditions of thermal equilibrium.

Silaformyl anions labeled with ^{29}Si were obtained by selecting m/z 48 ($H_3{}^{29}SiO^-$) in the SIFT quadrupole and dissociating this ion to $H^{29}SiO^-$ upon injection. In order to obtain the silaformyl anion labeled with ^{18}O, small amounts of $H_2{}^{18}O$ were ionized to produce $H^{18}O^-$ in the first flow tube, phenylsilane was introduced downstream, and m/z 49 ($H_3Si^{18}O^-$) was selected for dissociation.

All reactions were studied at 300 K at a helium buffer gas pressure of 0.5 Torr and a flow of 250 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 detection orifice. A calibration curve was generated by using a series of ions of masses similar to those of the product ions.[13] Hydroxide (m/z 17), methoxide (m/z 31), formate (m/z 45), acetate (m/z 59), and propionate (m/z 73) ions were used to calibrate the lower masses; the M - 1 ions of fluorobenzene and pentafluorobenzene were used for the higher masses. 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) with use of a measured flow of the neutral reagent. Reported values are the average of three measurements with different flows and are reproducible to within 10%.

Table II. Calculated Geometries and Vibrational Frequencies for $HSiO^-$ Isomers at the 6-31++G** Level

	geometry[a]		frequencies[b]			energy[c]
$HSiO^-$	Si–O	1.550 (1.602)	801	1045	1499	−364.344 808 (HF)
	Si–H	1.598 (1.596)				−364.645 731 (MP2)
	H–Si–O	106.8 (106.3)				−364.647 865 (MP2)[d]
$SiOH^-$	Si–O	1.721	668	858	3820	−364.295 154 (HF)
	O–H	0.939				−364.578 730 (MP2)
	Si–O–H	111.5				

[a] Distances in Å and angles in deg. Values in parentheses are from optimization at the MP2/6-31++G** level. [b] Frequencies in cm^{-1} scaled by 0.9. [c] Total energy in hartrees corrected for zero-point vibrational energies (HF/6-31++G**) scaled by 0.9. Correction for $HSiO^-$ is 0.007622 hartree and for $SiOH^-$ it is 0.012180 hartree. HF refers to HF/6-31++G**//HF/6-31++G** and MP2 refers to MP2/6-31++G**//HF/6-31++G**. [d] MP2/6-31++G**//MP2/6-31++G**.

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%), Ar (99.95%), CO_2 (99.5%), SO_2 (99.9%), and COS (97.7%). Other reagents also were obtained from commercial sources and were purified as necessary before use. The helium buffer gas was passed through a liquid-nitrogen-cooled molecular sieve trap before entering the flow tubes.

Results

The results of the reactions of the silaformyl anion with the neutral reagents we have investigated are given in Table I. The structures of the product ions are those deduced from their mass, from labeling studies, and by analogy with other processes. In all cases more than one product ion is formed, and the branching ratio among the observed reaction channels is also given in the table. For each reaction the overall rate constant for the disappearance of the silaformyl anion is given. In the gas phase, ions and neutrals are attracted to one another by ion–dipole and ion induced–dipole forces so that their collision rates depend upon the masses and structures of the reaction partners. To compare the reactivities of an ion toward a series of neutrals it is more revealing to compare reaction efficiencies, i.e. reactions per collision,[14] than reaction rates themselves.

Ion Structure. An anion containing one silicon, one oxygen, and one hydrogen atom can have two structures, $HSiO^-$ and $HOSi^-$. The method of synthesis of the ion and its chemical reactions are best in accord with the former structure. Nevertheless, since so little is known about the chemistry of such species we turned to an analysis of the relative energies of the two species by ab initio molecular orbital methods. The anion structures were optimized at the Hartree-Fock level with GAUSSIAN 82[15] with a 6-31++G** basis set,[16] which includes diffuse orbitals to accommodate the negative charge. At the MP2/6-31++G**//6-31G** level, including zero-point energy corrections scaled by 0.9,[17] $HSiO^-$ is calculated to be more stable than $HOSi^-$ by more than 40 kcal/mol (Table II). Further details of these computations, as well as a detailed study of the neutral parent compound, will be reported separately.[18] In the interim, it seems clear that

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(12) The 50 V is the potential difference between the ion source and the injector plate. The exact kinetic energy of the ions is sensitive to other factors and is not well characterized.

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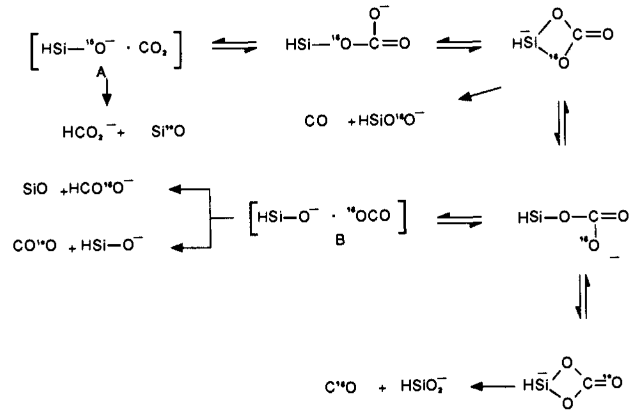
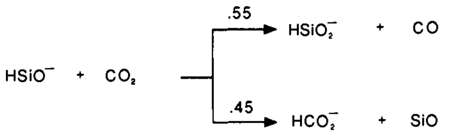
(18) Ion and neutral computations will be published separately in collaboration with Professor M. S. Gordon. Various computations on the neutral parents, HSiOH and $H_2Si{=}O$, have been published as follows: (a) Kudo, T.; Nagase, S. *Organometallics* **1986**, *5*, 1207. (b) Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1986**, *128*, 507. (c) Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589. (d) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833. (e) Kudo, T.; Nagase, S. *J. Organomet. Chem.* **1983**, *253*, C23.

Scheme I



the calculated differences are so large that it is extremely unlikely that the order of stability between the two ions could be reversed by calculations at still higher levels of theory. An optimization including correlation effects was undertaken for $HSiO^-$ and these results also are reported in Table II.

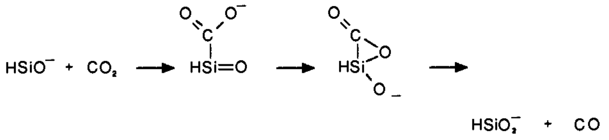
Reactions with CO_2. $HSiO^-$ (m/z 45) reacts relatively rapidly with CO_2 with the appearance of a new peak, at m/z 61, in the spectrum. However, only about half of the initial m/z 45 signal can be removed even at high CO_2 flows, which suggested that an ion of this mass is formed as a product. Indeed when $^{13}CO_2$ was used as the neutral reagent the m/z 45 ion could be reacted away entirely with the formation of m/z 46 and 61 peaks in a 45:55 ratio. We formulate these two products as the formate and silaformate ion respectively, as shown in eq 3. Hydride transfer from an anion to CO_2 is a common process in the gas phase, and indeed the formyl ion also reduces CO_2 to the formate ion (eq 4).[19] However, oxygen atom transfer from CO_2 is uncommon and we felt further investigation of its mechanism was warranted especially since such a study might throw light on how the $HSiO^-$ ion interacts with an electrophile. By analogy with its carbon analogue the silicon atom in $HSiO^-$ might act as a nucleophile, adding to the carbonyl carbon. Oxygen atom transfer could then occur by way of a three-membered ring with expulsion of carbon monoxide (eq 5). A second conceivable pathway for oxygen transfer would be by direct oxygen abstraction by the silicon atom acting as a silylene (eq 6). An analogy for such a process in the gas phase is found in our work on carbene anions derived from diazomethane (eq 7).[20] Finally, the reaction might be initiated by nucleophilic attack by oxygen on the carbonyl carbon followed by oxygen transfer through a four-membered ring (eq 8). Such processes have been suggested previously for oxygen exchange in the reaction of the silamethoxide ion with labeled CO_2 (eq 9)[10] and in the reaction between the silaacetylide anion and CO_2 (eq 10).[6c]



(3a)

(3b)

$$HCO^- + CO_2 \longrightarrow HCO_2^- + CO \qquad (4)$$



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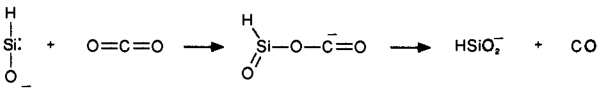


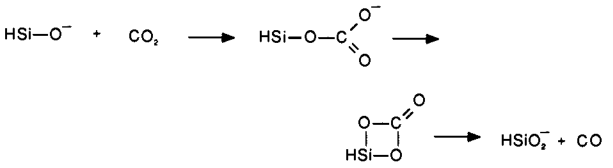
(6)

$$^-OOC{-}CH{:} + O{=}C{=}O \longrightarrow {}^-OOC{-}CH{=}O + CO \qquad (7)$$

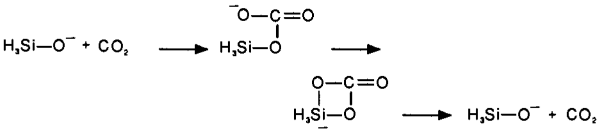
Table III. Results of Isotopically Labeled Experiments

reagents	products	distribution of label obs	distribution of label stat
$HSiO^- + {}^{13}CO_2$	$H^{13}CO_2^-$		
	$HSiO_2^-$		
$HSi^{18}O^- + CO_2$[a]	$HSi^{16}O^-$		
	$HSi^{18}O^{16}O^-:HSi^{16}O_2^-$	3.7:1	2:1
	$HC^{16}O_2^-:HC^{18}O^{16}O^-$	2.4:1	1:2
$HSi^{18}O^- + COS$[b]	$HSi^{16}O^-$		
$HSi^{18}O^- + SO_2$	$HS^{16}O_2^-$		
	$S^{16}O_2^-$		
	$HSi^{18}O^{16}O^-:HSi^{16}O_2^-$	2.6:1	2:1
$HSi^{18}O^- + O_2$	$Si^{18}O^{16}O^-$		
	$HSi^{18}O^{16}O^-$		
	$Si^{18}O^{16}O_2^-$		
$HSiO^- + CH_3CO_2D$	$HSiO_2^-:DSiO_2^-$	1.0:1	1:1
	$CH_3CO_2^-$		
$HSi^{18}O^- + CH_3CO_2H$	$HSi^{18}O^{16}O^-$		
	$CH_3C^{16}O_2^-$		
$HSiO^- + CD_3NO_2$	$HSiO_2^-$		
	$HSiO_3^-$		
	$CD_2NO_2^-$		
$HSi^{18}O^- + CH_3NO_2$	$HSi^{18}O^{16}O^-$		
	$HSi^{18}O^{16}O_2^-$		
	$CH_3N^{16}O_2^-$		

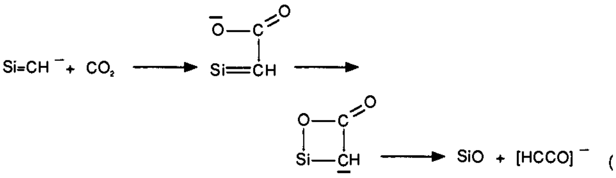
[a] $HSi^{16}O^-$ represents 5% of the total product. [b] $HSi^{16}O^-$ represents 5% of the total product. The isotopic content of the other products could not be determined.



(8)



(9)



(10)

In order to distinguish among these pathways we examined the reaction of the anion labeled with oxygen-18. Extensive but not complete scrambling of the three oxygen atoms was found. A small amount of unlabeled $HSiO^-$ is produced and nearly one-quarter of the $HSiO_2^-$ ions contain none of the label. Our results, which are summarized in Table III, are best accounted for by nucleophilic oxygen attack as shown in Scheme I. It should be noted that throughout this paper we have used square brackets to denote ion–molecule complexes. The initially formed ion–molecule complex A can transfer a hydride or the oxygen can add to the carbonyl carbon. This adduct can cyclize and either lose CO to form the silaformate ion or reopen, equilibrating two of the oxygen atoms. Because unlabeled $HSiO^-$ and labeled $HCOO^-$ are produced, this adduct must, at least in part, form another

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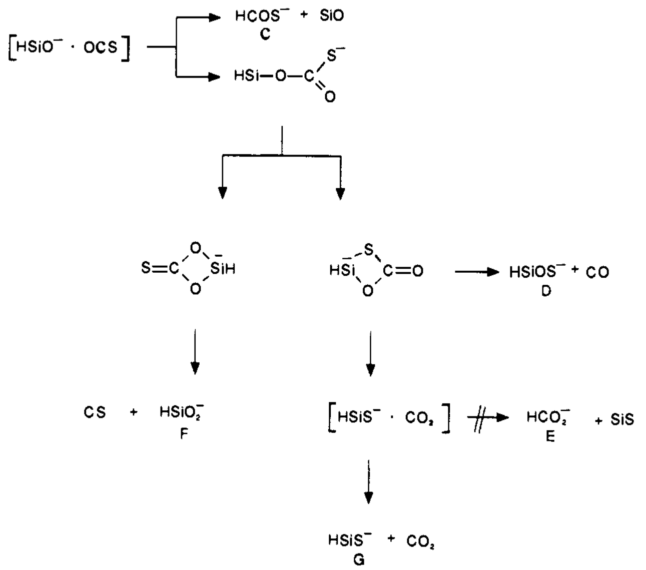
[19] Kleingeld, J. C.; Ingemann, S.; Jalonen, J. E.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1983**, *105*, 2474.

[20] DePuy, C. H.; Van Doren, J. M.; Gronert, S.; Kass, S. R.; Motell, E. L.; Ellison, G. B.; Bierbaum, V. M. *J. Org. Chem.* **1989**, *54*, 1846.

Scheme II



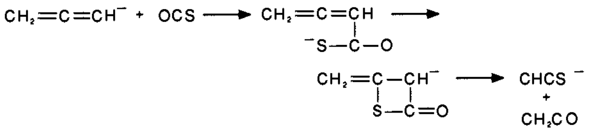
ion–dipole complex B from which dissociation and hydride transfer can occur.

If ring formation and ring opening were rapid processes compared to loss of carbon monoxide, equilibration among all three oxygens would be observed and labeled and unlabeled silaformate ions would be formed in the statistical ratio of 2:1. The observed ratio of 3.7:1 indicates that the processes occur at comparable rates. Dissociation of the adduct back to ion–dipole complex A must also occur on a comparable time scale, since approximately one-third of the formate ion contains labeled oxygen.

Reaction with OCS. On the basis of the CO_2 reaction, we would expect $HSiO^-$ to react with OCS by hydride transfer and by addition of oxygen to the carbonyl carbon. Cyclization could occur either through oxygen or through sulfur. The various possibilities are shown in Scheme II. When $HSiO^-$ is allowed to react with COS, two ions are observed, one at *m/z* 77 (15%) and one at *m/z* 61 (85%). The former we assign to the product of sulfur atom transfer, HSiOS. The latter is a mixture of three ions all having *m/z* 61: $HSiS^-$ (65%), $HCOS^-$ (20%), and $HSiO_2^-$ (trace).

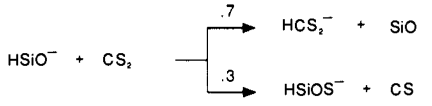
We used isotopic tracers to probe these isomeric ions and obtain approximate product ratios. In order to distinguish the silicon-containing ions from $HCOS^-$, we generated $H^{29}SiO^-$ by selecting the naturally abundant (4.7%) $H_3{}^{29}SiO^-$ and dissociating it upon injection. Reaction of the resulting $H^{29}SiO^-$ with OCS gave $H^{29}SiO_2^-$ (F) and $H^{29}SiS^-$ (G) as well as approximately 25% of the original *m/z* 61. Therefore, about 20% of the total product ions result from hydride transfer to form $HCOS^-$ (C). To distinguish between the two silicon-containing ions we produced and injected $H_3Si^{18}O^-$, dissociated it to $HSi^{18}O^-$, and allowed it to react with OCS. Only a trace of ionic product at *m/z* 63 was formed, indicating that $HSiO_2^-$ is at best a minor product. Thus the main products of the reaction of $HSiO^-$ with OCS are $HSiS^-$ (65%), $HCOS^-$ (20%), and $HSiOS^-$ (15%).

In comparing the products of the reactions of $HSiO^-$ with CO_2 and OCS, we note that in the latter reaction most of the ions have made it completely through the reaction scheme and formed $HSiS^-$; this would correspond in the CO_2 reaction to complete equilibration of the label from $HSi^{18}O^-$ to $HSiO^-$. However, we observed only a small amount of $HSiO^-$ in the reaction of COS with $HSi^{18}O^-$. Several factors must help account for the difference. Note that no HCO_2^- is produced in the reaction with OCS. This suggests that the hydride affinity of CO_2 is smaller than that of SiS so that $HSiS^-$ cannot hydride transfer to CO_2. Since $HSiO^-$ does hydride transfer extensively to CO_2, much less $HSiO^-$ is formed. Second, the formation of $HSiS^-$ and CO_2 from $HSiO^-$ and OCS must be exothermic, thus driving the reaction in the observed direction. Oxygen exchange is, of course, thermoneutral. First, at least in the carbon analogues of rearrangements involving CO_2, OCS, and CS_2, sulfur seems to participate in rearrangement more readily than oxygen. For example, the following rearrangement is observed upon reaction of the allenyl anion with COS, but an analogous rearrangement does not take place with CO_2.[21]



(11)

Reaction with CS_2. When CS_2 is allowed to react with $HSiO^-$ only a single peak, at *m/z* 77, is observed in the mass spectrum. An ion of this mass could arise either from hydride transfer to CS_2 to form HCS_2^- or by sulfur atom transfer to form $HSiOS^-$. To distinguish between these two possible products we prepared $H^{29}SiO^-$ and allowed it to react with CS_2; two peaks *m/z* 77 and 78, were obtained in an approximately 2.5:1 ratio (eq 12). From

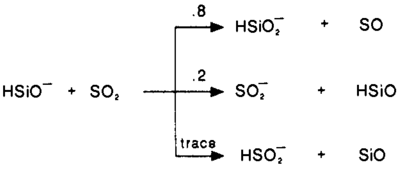


(12a)

(12b)

these results we can see that, if we assume the possibility of a series of reactions like those in Scheme I or II, only the first one or two steps have occurred before dissociation to products. As noted previously, reactions with CS_2 are more exothermic than those of OCS or CO_2.[21] Hydride transfer occurs more readily, and addition results in an ion with more internal energy, leading to more rapid decomposition. The results then, while not necessarily predictable, are at least consistent with our earlier work.

Reaction with SO_2 and O_2. Electron transfer (20%) and oxygen transfer (80%) are the major pathways for reactions of $HSiO^-$ with SO_2. A trace of hydride transfer is also observed (eq 13).

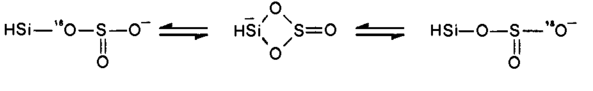


(13a)

(13b)

(13c)

The observation of electron transfer places an upper limit of 1.1 eV on the electron affinity[22] of the silaformyl radical HSiO. When $HSi^{18}O^-$ is used as the reactant ion, the observed SO_2^- and HSO_2^- are both unlabeled, but $HSiO_2^-$ and $HSiO^{18}O^-$ are produced in a 2.6:1 ratio (complete scrambling of the oxygens would, as before, give a 2:1 ratio). Clearly a cyclic intermediate is formed that can open in competition with loss of SO (eq 14). Hydride and electron



(14)

transfer must occur before such a cyclic intermediate is formed since the ions resulting from such processes contain no labeled oxygen. Once the cyclic intermediate is formed it does not dissociate, since no unlabeled $HSiO^-$ is observed among the products.

Reaction of $HSiO^-$ with O_2 is rapid and leads to the formation of a number of product ions, $HSiO_2^-$, SiO_2^-, and SiO_3^-. When $HSi^{18}O^-$ is used no scrambling of oxygen atoms in any of the product ions is observed. These results are best accounted for by initial attack of the silicon atom on O_2 rather than by attack by the oxygen atom. This is reasonable since O_2 is not normally susceptible to nucleophilic attack while the silicon atom is electron deficient. The products can plausibly be thought to arise by cleavage of the O–O bond in the initial adduct to form $HSiO_2^-$ and an oxygen atom that can either escape (eq 15a), abstract a hydrogen atom (eq 15c), or add to the silicon with subsequent loss of a hydrogen atom (eq 15b).

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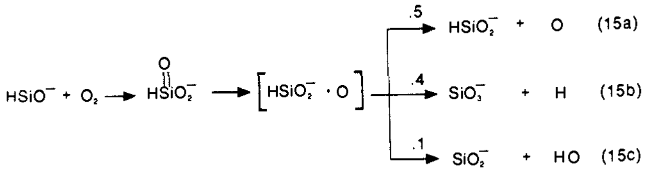
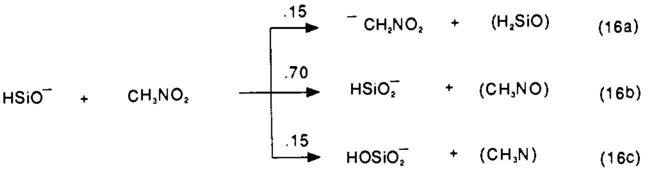
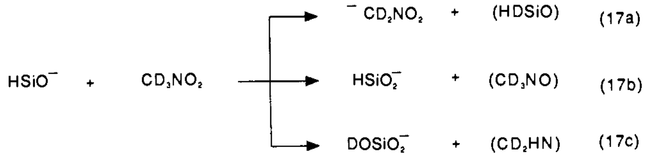
(21) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556.

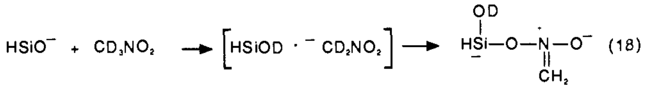
(22) The electron affinity of SO_2 is 1.1 eV: Grabowski, J. J.; Van Doren, J. M.; DePuy, C. H.; Bierbaum, V. M. *J. Chem. Phys.* **1984**, *86*, 575.



Reaction with CH_3NO_2 and CH_3COOH. Three product ions are formed upon reaction of $HSiO^-$ with nitromethane, one resulting from proton transfer and the other two arising from one and two oxygen atom transfers, respectively (eq 16). In the equations that follow, we have shown that neutral products in parentheses to denote only their empirical formulae, not their structures. No oxygen exchange is observed in any of the product ions when $HSi^{18}O^-$ is used as the reactant. There is, however, very specific labeling among the product ions when deuterated nitromethane is used as the neutral reagent (eq 17). These results are best accommodated if the initial reaction is deuteron transfer from the nitromethane to the oxygen atom of the silaformyl anion, and this suggests that the silylene form of the conjugate acid, HSiOH, is more stable than the silaformaldehyde form H_2SiO although it is, of course, possible that there is a kinetic barrier to protonation at silicon.[23] In this way the hydrogen and deuterium atoms remain distinct. Several pathways can be written for the subsequent transfer of the oxygen atoms, beginning with attack of the nucleophilic oxygen of the nitromethane anion on the silicon atom.

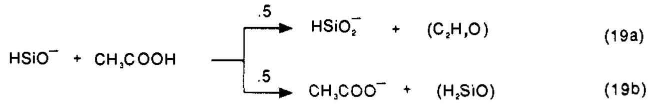


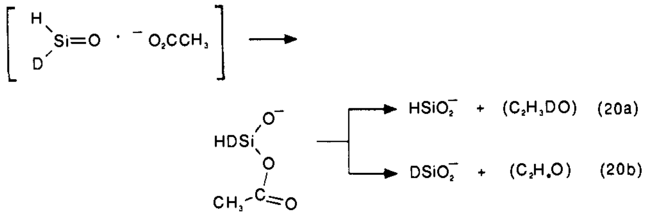




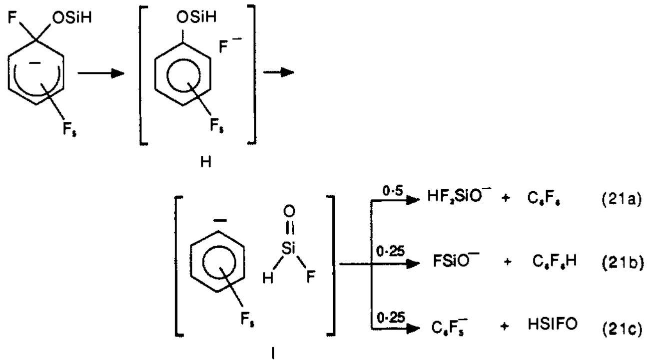
Some support for this mechanism is found in the observations that there is a small (10%) reduction in the rate of reaction of the deuterionitromethane as compared to that of nitromethane itself and that $(CH_3)_3CNO_2$, which contains no acidic hydrogens, reacts still slower (by a factor of 4) and only $HSiO_2^-$ is formed.

Another manifestation of the great oxygen affinity of the silaformyl anion is shown by its reaction with acetic acid to form the silaformate ion and, presumably, acetaldehyde (eq 19). When CH_3COOD is used as the neutral reagent an equal mixture of $HSiO_2^-$ and $DSiO_2^-$ is formed. This result suggests the formation of the silaformaldehyde form of H_2SiO so that one hydrogen and deuterium become equivalent. An equivalent result would be obtained if $HSiO^-$, acting as a silylene, inserts into the O–D bond of CH_3COOD. However, since $HSiO^-$ does not react with alcohols, this appears unlikely. This postulation of oxygen protonation by nitromethane and silicon protonation by acetic acid is not inconsistent; acetic acid is 9 kcal/mol more acidic than nitromethane and so may be capable of protonation on the less acidic site of the anion.

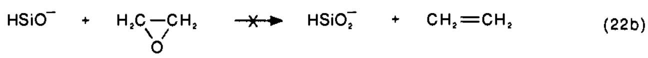




Reaction with Other Reagents. Hexafluorobenzene has often been used as a neutral reagent in ion–molecule reactions because of its great reactivity toward nucleophiles.[24] It reacts rapidly with $HSiO^-$ to form three ionic products as shown in eq 21. We formulate these products as arising from initial nucleophilic attack on the benzene ring by oxygen. Loss of fluoride would give the ion–dipole complex H from which fluoride attack on silicon would lead to a second ion–dipole complex I. The three observed ionic products could arise from this complex, by dissociation or proton or fluoride transfer. It is remarkable that the major product is the result of the abstraction of two fluorine atoms from hexafluorobenzene suggesting that the fluoride affinity of HFSi=O is very high.



Despite these reactions, $HSiO^-$ is not indiscriminately reactive. For example, it does not react with N_2O or with ethylene oxide even though highly exothermic pathways are possible (eq 22).[25] This lack of reactivity is consistent with previous work on both N_2O and ethylene oxide.[26]



Thermochemistry of Silaformaldehyde and Silaformyl Anion. Given that the gas phase heat of formation of SiO is known,[27] the heat of formation of $HSiO^-$ may be determined by allowing it to react with a series of compounds of known hydride affinity (HA).[28] In this way the hydride affinity of SiO may be bracketed.

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(23) Published high-level ab initio calculations predict similar stabilities for H_2SiO and HSiOH, see ref 18. Recent computations at the MP4/MC-311G(d,p) level show that H_2SiO is more stable than HSiOH by 2.7 kcal/mol; personal communication from M. S. Gordon.

(24) For example, see: Briscese, S. M.; Riveros, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 230.

(25) Oxidation of $HSiO^-$ is observed with COS and the similar process with N_2O is over 100 kcal mol^{-1} more exothermic: COS → O + CS (ΔH° = 161.6 kcal mol^{-1}); $N_2O \rightarrow O + N_2$ (ΔH° = 40.5 kcal mol^{-1}). The reduction of ethylene oxide is 75 kcal mol^{-1} more exothermic than the observed reduction of COS: $C_2H_4O \rightarrow O + C_2H_4$ (ΔH° = 85.7 kcal mol^{-1}).

(26) (a) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849. (b) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800. (c) DePuy, C. H.; Beedle, E. C.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1982**, *104*, 6483. (d) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229.

(27) Heats of formation of neutral compounds were taken from the following: (a) JANAF Tables: 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*, Supplement No. 1. (b) Pedly, J. B.; Rylance, J. *Sussex-N. P. L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, England, 1977.

Although $\mathrm{HSiO^-}$ will not transfer a hydride to acetone (HA = 39.6 kcal mol^{-1}), acetaldehyde (HA = 40.7 kcal mol^{-1}), or benzaldehyde (HA = 45.9 kcal mol^{-1}), hydride transfer to acrylonitrile (HA = 57.6 kcal mol^{-1}) and acrolein (HA = 61.5 kcal mol^{-1}) is observed. Hydride transfer to $\mathrm{CO_2}$ (HA = 51.6 kcal mol^{-1}) leads to an ion of mass 45, the same mass as $\mathrm{HSiO^-}$; however, experiments with $\mathrm{^{13}CO_2}$ resulted in an ion of mass 46 ($\mathrm{H^{13}CO_2^-}$) indicating hydride transfer. Therefore, the hydride affinity of SiO is somewhere between that of $\mathrm{CO_2}$ and benzaldehyde and may be assigned a value of 49 ± 5 kcal mol^{-1}. By eq 23, the $\Delta H^\circ_f(\mathrm{HSiO^-})$ is determined to be −38 ± 5 kcal mol^{-1}.

$$\Delta H^\circ_f(\mathrm{HSiO^-}) = -\mathrm{HA(SiO)} + \Delta H^\circ_f(\mathrm{SiO}) + \Delta H^\circ_f(\mathrm{H^-}) \quad (23)$$

It is interesting to compare the hydride affinity of SiO (HA = 49 kcal mol^{-1}) with that of the isoelectronic carbon analogue, CO (HA = 8 kcal mol^{-1}). Although the hydride in $\mathrm{HCO^-}$ is barely bound, the hydride in $\mathrm{HSiO^-}$ is bound more strongly than those in simple alkoxides such as $\mathrm{CH_3CH_2O^-}$ (HA = 40.7 kcal mol^{-1}). This gives evidence of the clear difference between C=O and Si=O species. Obviously, SiO is much more willing than CO to accept the hydride at the expense of a π-bond to oxygen.

It also is possible to bracket the proton affinity of the $\mathrm{HSiO^-}$ anion and, as a result, determine the heat of formation of its parent ($\mathrm{H_2SiO}$ or HSiOH).[29] This procedure is complicated because we have a minor $\mathrm{H_3SiO^-}$ contamination, and $\mathrm{HSiO^-}$ reacts with standard acids in ways other than proton transfer. Proton abstraction from acetic acid ($\Delta G^\circ_{\mathrm{acid}}$ = 341 kcal mol^{-1}), cyclopentadiene (ΔG_{acid} = 348 kcal mol^{-1}), and nitromethane ($\Delta G^\circ_{\mathrm{acid}}$ = 350 kcal mol^{-1}) is observed, and a lower limit of 350 kcal mol^{-1} can be placed on the acidity of the parent compound. Because $\mathrm{HSiO^-}$ does not react with acetone, we can set an upper limit of 362 kcal mol^{-1} on its acidity. Reactions with compounds of intermediate acidity led to inconclusive results; therefore, we must report the proton affinity of $\mathrm{HSiO^-}$, $\Delta G^\circ_{\mathrm{acid}}$ = 356 ± 8 kcal mol^{-1} with large error bars. Taking the proton affinity and the heat of formation of $\mathrm{HSiO^-}$, the heat of formation of $\mathrm{H_2SiO}$ (HSiOH) may be estimated with eq 24.[30] The value obtained in this way,

$$\Delta H^\circ_f(\mathrm{H_2SiO,\ HSiOH}) = \Delta H^\circ_f(\mathrm{HSiO^-}) + \Delta H^\circ_f(\mathrm{H^+}) - \Delta H^\circ_{\mathrm{acid}}(\mathrm{HSiO^-}) \quad (24)$$

$\Delta H^\circ_f(\mathrm{H_2SiO,\ HSiOH})$ = −36 ± 10 kcal mol^{-1}, corresponds to the heat of formation of the more stable isomer assuming that protonation at silicon and oxygen are both kinetically viable.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation under Grants CHE-8615808 (R.D.) and CHE-8815459 (C.H.D.). In addition, C.H.D. acknowledges the Alexander von Humboldt-Stiftung for a Senior U.S. Scientist Award and the Institut für Organische Chemie der Technischen Universität Berlin for hospitality while part of this work was accomplished.

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(28) Hydride affinities are taken from a compiliation provided by Squires, R. R., Purdue University. See: Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139.

(29) Proton affinities and heats of formation of anions are taken from the following: 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*, Supplement No. 1.

(30) The free energy of protonation may be converted to an enthalpy by estimating the entropy of protonation, see: Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed., Academic Press: New York, 1979; Vol. 2.

Subpicosecond Fluorescence Anisotropy Studies of Tryptophan in Water

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Received May 19, 1989

Abstract: Ultraviolet fluorescence upconversion optical gating has been used to measure the excitation and emission wavelength dependence of the fluorescence depolarization of tryptophan in water with subpicosecond resolution. An initial anisotropy of 0.4 is observed for the first time. The short time decay behavior is found to be complicated by non-rotational contributions to the anisotropy decay arising from the interaction of the two low-lying ^1L_a and ^1L_b excited states. The time constant for ^1L_b to ^1L_a internal conversion is found to be 1.6 ± 0.2 ps. A generalized version of the level kinetics model of Cross et al.[29] is found to adequately describe the fluorescence anisotropy decay dependence on excitation and emission wavelength. The anisotropy data are interpreted in terms of a model for tryptophan fluorescence depolarization that includes the effects of vibronic coupling and vibrational relaxation. Our results indicate that the fluorescence anisotropy will be an ambiguous method of studying protein motion for times less than 5–10 ps.

For more than three decades, the electronic spectroscopy and photophysics of tryptophan and its derivatives in solution have been the subject of intense study.[1-3] This effort has been motivated by the desire to understand the near-ultraviolet absorption and fluorescence properties of tryptophanyl residues in proteins and establish a basis for their use as intrinsic probes of protein structure and conformational dynamics.[4-7] An accurate characterization of the short time fluorescence anisotropy behavior of tryptophan has become particularly important. Molecular dynamics simulations of small proteins have suggested that sig-

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[*] Address correspondence to this author at the Department of Chemistry.

[†] Department of Physics.

(1) Creed, D. *Photochem. Photobiol.* **1984**, *39*, 537.

(2) Konev, S. V. *Fluorescence and Phosphorescence of Proteins and Nucleic Acids*; Plenum: New York, 1967.

(3) Longworth, J. W. In *Excited States of Proteins and Nucleic Acids*; Steiner, R. F., Weinryb, I., Eds.; Plenum: London, 1971; p 319.

(4) Longworth, J. W. In *Time-Resolved Fluorescence Spectroscopy in Biochemistry and Biology*; Cundall, R. B., Dale, R. E., Eds.; Plenum: London, 1983.

(5) Beechem, J. M.; Brand, L. *Annu. Rev. Biochem.* **1985**, *54*, 43.

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