

it is systematically lower may arise from the possibility that there is a small contribution from wall reactions. At the 10% level these would be difficult to detect. In addition, in many of the studies it was assumed that the back reaction had an activation energy of 1 ± 1 kcal/mol. It now seems much more likely that these

are actually in the range 0 to 0.5 kcal/mol.¹⁹

Acknowledgment. This work has been supported by grants from the National Science Foundation (CHE-86-46942) and the U.S. Army Research Office (DAAG29-85-K-0019).

Gas-Phase Reactions of Si⁺(²P) with Hydrogen Cyanide, Acetonitrile, Cyanogen, and Cyanoacetylene: Comparisons with Reactions of C⁺(²P)

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Abstract: Reactions of ground-state Si⁺(²P) ions have been investigated with the cyanide molecules HCN, CH₃CN, C₂N₂, and HC₃N at 296 ± 2 K with the selected-ion flow tube (SIFT) technique. All four cyanides were observed to form adduct ions with Si⁺ in one reaction channel, but otherwise the nature and degree of reactivity were found to be strongly dependent on the nature of the substituent. Si–N bond formation in the bimolecular products prevailed with HCN and C₂N₂, while Si–C bond formation was predominant with CH₃CN and HC₃N. These primary reactions as well as several observed secondary reactions are discussed as sources for neutral molecules such as CNSi, SiCH, SiC₂, and other, more complex, silicon-bearing molecules in partially ionized interstellar gas clouds. Results of quantum chemical calculations performed at the MP4SDTQ/6-31G**//6-31G** level are presented which provide insight into the possible structure of the adduct ion between Si⁺ and HCN. The reactivities observed with Si⁺ are compared with those available for the analogous reactions of C⁺ proceeding under similar conditions of temperature and pressure. The reactions with Si⁺ are uniformly slower and less efficient than the corresponding reactions of C⁺, and the competition with adduct formation is not apparent for the reactions of C⁺. These differences in reactivity are rationalized in terms of perceived differences in the potential energy profiles.

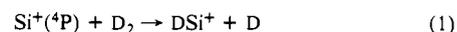
The growing interest in fundamental aspects of the chemical bonding of atoms to silicon,¹ and the importance of silicon-bearing compounds in the chemistry of interstellar gas clouds,^{2,3} recently has prompted us to conduct systematic investigations of ion chemistry initiated by atomic silicon ions in their ground electronic state in the gas phase. We have established previously that the chemistry initiated by atomic silicon ions reacting with molecules containing hydroxyl groups can lead to molecules containing silicon–oxygen double bonds.⁴ Also, we have found that reactions of atomic silicon ions with ammonia and methylamines can lead to the formation of molecules such as SiNH, SiNCH₃, and H₂SiNH in which silicon is doubly bonded with nitrogen.^{5,6} Here we monitor the response of atomic silicon ions to molecules containing the triply bonded C≡N substituent in an attempt to identify further routes to Si–N bond formation and to explore the competition with Si–C bond formation. The kinetics and product distributions are investigated for reactions of Si⁺(²P) with hydrogen cyanide, acetonitrile, cyanoacetylene, and cyanogen. These particular cyanides were chosen as substrates, in part because of their importance in the chemistry of interstellar gas clouds.^{2,3}

A second incentive for this investigation was provided by the availability of experimental results for the gas-phase reactions of the four cyanides selected for study with atomic carbon ions in their ground electronic state. These results presented a unique

opportunity to compare the reactivities of the group IV atomic ions Si⁺(²P) and C⁺(²P). The comparison is possible without complications due to charge transfer. The relatively low electron recombination energies of these two atomic ions, 8.151 eV for Si⁺ and 11.260 eV for C⁺, ensures that thermal collisions with the cyanides do not lead to charge transfer (due to endothermicity) while still permitting chemical bond formation channels. Differences in the chemical reactivities of these two atomic ions are expected from the substantial difference in their enthalpy of formation, 136 kcal mol⁻¹ at 298 K, and should be manifested in the nature of these bond formation channels and their relative efficiencies. Differences also may be expected to appear in the overall reaction efficiencies.

Experimental Section

All measurements were performed with the selected-ion flow tube (SIFT) apparatus which has been described in detail elsewhere.^{7,8} Atomic silicon ions were derived from a 2–3% mixture of tetramethylsilane in deuterium by electron impact at 50–100 eV. The deuterium was added to scavenge the metastable Si⁺(⁴P) ions in the source with the following reaction:⁴



The isotope of Si⁺ at $m/e = 28$ was selected and introduced into helium buffer gas at 0.35 Torr or 1.15×10^{16} He atoms cm⁻³. Neutral reagents were added downstream. Primary and secondary ions were monitored as a function of the added neutral reagent. Rate constants and product distributions were derived from these observations in the usual manner.^{7,9} No attempt was made to investigate the pressure dependence of rate

(1) Raabe, G.; Michl, J. *J. Chem. Rev.* **1985**, *85*, 419.

(2) Turner, J. L.; Dalgarno, A. *Astrophys. J.* **1977**, *213*, 386.

(3) Millar, T. J. *Astrophys. Space Sci.* **1980**, *72*, 509.

(4) Włodek, S.; Fox, A.; Bohme, D. K. *J. Am. Chem. Soc.* **1987**, *109*, 6663.

(5) Włodek, S.; Rodriguez, C. F.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Chem. Phys. Lett.* **1988**, *143*, 385.

(6) Włodek, S.; Bohme, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2396.

(7) Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion. Phys.* **1980**, *36*, 259.

(8) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *55*, 69.

(9) Adams, N. G.; Smith, D. J. *Phys. B* **1976**, *9*, 1439.

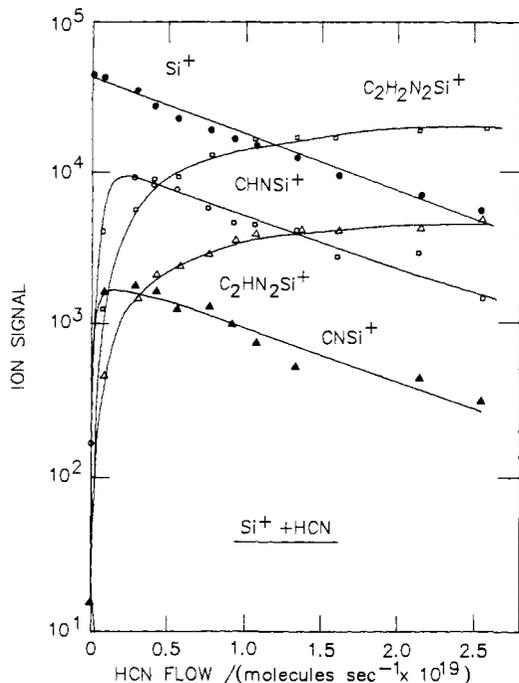


Figure 1. Observed variations in the ion signals recorded for the addition of hydrogen cyanide into the reaction region of the SIFT apparatus in which Si^+ is initially established as the dominant ion in helium buffer gas: $P = 0.35$ Torr, $\bar{v} = 6.4 \times 10^3$ cm s $^{-1}$, $L = 46$ cm, and $T = 294$ K.

Table I. Rate Constants (in Units of 10^{-10} cm 3 molecule $^{-1}$ s $^{-1}$), Product Distributions, and Efficiencies for Reactions of $\text{Si}^+(^2P)$ with Several Cyanides at 296 ± 2 K

reaction	neutral reactant	products	product distributn ^a	k_{exp}^b	k_{exp}/k_c^c
2a	HCN	CHNSi $^+$	0.8	0.070	0.0020
2b		CNSi $^+$ + H	0.2		
3a	NCCN	CNSi $^+$ + CN	0.55	1.5	0.12
3b		C $_2$ N $_2$ Si $^+$	0.45		
4a	CH $_3$ CN	CH $_2$ Si $^+$ + CHN	0.5	24	0.53
4b		C $_2$ H $_3$ NSi $^+$	0.5		
5a	HC $_2$ CN	C $_2$ HNSi $^+$ + CN	0.7	14	0.34
5b		C $_3$ HNSi $^+$	0.3		

^a Primary product ions which contribute 5% or more. The product distributions have been rounded off to the nearest 5% and are estimated from experimental repetition to have a relative accuracy of within $\pm 30\%$. ^b The effective bimolecular rate constant is given at a total pressure of 0.35 Torr and a helium density of 1.15×10^{16} atoms cm $^{-3}$. The accuracy of the rate constants is estimated to be better than $\pm 30\%$. ^c k_{exp}/k_c is a measure of reaction efficiency. Collision rate constants, k_c , are derived from the combined variational transition-state theory/classical trajectory study of Su and Chesnavich.¹²

constants and product distributions. The helium buffer gas and the reagent gases CH $_3$ CN and C $_2$ N $_2$ were of high purity (>99.5 mol%). HCN and HC $_3$ N were synthesized according to established laboratory procedures and used without further purification.^{10,11} Previous experiments with H $_3^+$ as the "chemical ionization" reagent indicated a purity for these two gases produced in this manner of greater than 99%. All measurements were made at an ambient temperature of 296 ± 2 K.

Experimental Results

Table I summarizes the rate constants and product distributions observed for the reactions of $\text{Si}^+(^2P)$ with the four different cyanide molecules investigated in this study. The experimental rate constants are compared with computed collision rate constants in order to provide a measure of reaction efficiencies. Collision rate constants are derived from the combined variational transition-state theory/classical trajectory study of Su and Chesnavich.¹² Polarizabilities and dipole moments were derived from

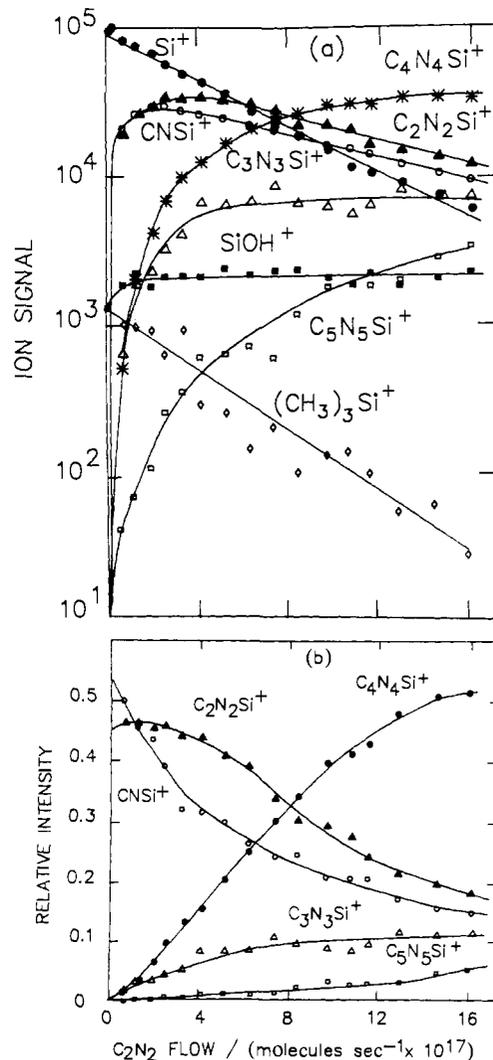


Figure 2. (a) Observed variations in the ion signals recorded for the addition of cyanogen into the reaction region of the SIFT apparatus in which Si^+ is initially established as the dominant ion in helium buffer gas: $P = 0.345$ Torr, $\bar{v} = 6.4 \times 10^3$ cm s $^{-1}$, $L = 46$ cm, and $T = 293$ K. Not shown are the profiles for ions at $m/e = 82$ and 184 which correspond to CN_3Si^+ and $\text{C}_6\text{N}_6\text{Si}^+$, respectively, and which rise at higher flows of cyanogen. (b) The fractional abundance of the product ions observed in (a). The intercepts at zero flow of cyanogen provide a measure of the initial product distribution, and the ion profiles provide further insight into the evolution of the products.

the usual sources.¹³ Thermochemical information was derived from the compilation of Rosenstock et al.¹⁴ unless indicated otherwise.

Hydrogen Cyanide. Figure 1 presents data which leads to the identification of the primary and secondary reactions initiated by atomic silicon ions in hydrogen cyanide. The apparent bimolecular rate constant for the primary reaction of Si^+ with HCN was found to be relatively small, $k = 7.0 \times 10^{-12}$ cm 3 molecule $^{-1}$ s $^{-1}$, and the main product was observed to be the adduct ion. About 20% of the reaction proceeds by H-atom elimination to yield CNSi $^+$. Both

(13) The polarizability of HCN, 2.59 Å 3 , was taken from the following: Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; John Wiley & Sons: New York, 1964. The polarizabilities for C $_2$ N $_2$ (5.01 Å 3), CH $_3$ CN (4.56 Å 3), and HC $_3$ N (5.29 Å 3) were derived from bond and group polarizabilities according to Lippencott and Stutman (Lippencott, E. R.; Stutman, J. M. *J. Phys. Chem.* **1964**, *68*, 2926). The dipole moments for HCN (2.98 D) and CH $_3$ CN (3.92 D) were taken from Nelsom et al. (Nelsom, R. D.; Lide, D. R.; Maryott, A. A. NSRDS-NBS 10, 1967), while that for HC $_3$ N (3.6 D) was taken from Westenber and Wilson (Westenber, A. A.; Wilson, E. B. *J. Am. Chem. Soc.* **1950**, *72*, 199).

(14) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Ser.* **6**, Suppl. 1 **1977**.

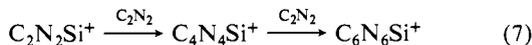
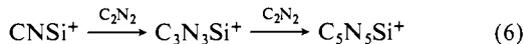
(10) Glemser, O. In *The Handbook of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic Press: New York, 1963; p 658.

(11) Moureu, C.; Bongrand, J. C. *Ann. Chim. (Rome)* **1920**, *14*, 47.

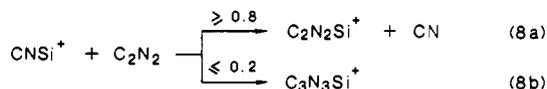
(12) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

of the product ions CHNSi⁺ and CNSi⁺ were seen to add HCN to form C₂H₂N₂Si⁺ and C₂HN₂Si⁺ ions, respectively. The effective bimolecular rate constants for these two addition reactions were found to be equal to $(3 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from a fit to the formation and loss curves for the CHNSi⁺ and CNSi⁺ ions.

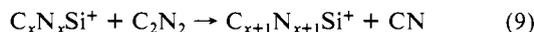
Cyanogen. Cyanogen was seen to react with Si⁺ much more efficiently than HCN, but the total reaction rate constant still is only about 10% of the collision limit. Experimental results for this system are shown in Figure 2 from which it is clearly seen that both primary product ions undergo sequential reactions with cyanogen to produce the family of ions C_xN_xSi⁺. Not shown in Figure 2 is an ion with a mass equal to that of C₆N₆Si⁺ which was observed at high flows of cyanogen. A superficial view of these results would attribute the formation of these ions to sequential addition reactions of the following type:



However, the evolution of the product ions shown in Figure 2b indicates that C₃N₃Si⁺ accounts for at most about 20% of the decay of CNSi⁺ which means that CNSi⁺ produces predominantly C₂N₂Si⁺ according to the following reaction:



The total rate constant for reaction 8 was determined from a fit to the CNSi⁺ profile to be equal to $(2.2 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Consequently it is conceivable that analogous reactions of the type



also contribute, at least for odd values of *x*.

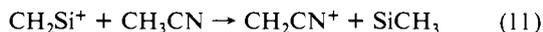
An ion with *m/e* = 82, presumably CN₃Si⁺, was observed to become the largest product ion at higher flows of cyanogen, $>1.5 \times 10^{19} \text{ molecules s}^{-1}$, apparently at the expense of C₄N₄Si⁺ which decayed with a slope corresponding to a rate constant of only about $7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. One possible source for CN₃Si⁺ is reaction 10:



However, it is also possible that faster reactions with impurities in the cyanogen, e.g., ClCN and HCN, contribute in an analogous fashion leaving C₄HN₂ and C₄ClN₂ as neutral products, respectively.

Acetonitrile. Elimination of HCN and adduct formation were observed to contribute equally to the reaction of Si⁺ with acetonitrile. The overall reaction proceeds at one half of the collision rate. Both of the primary ions CH₂Si⁺ and C₂H₃NSi⁺ were seen to attach a molecule of acetonitrile to form C₃H₅NSi⁺ and C₄H₆N₂Si⁺, respectively.

A secondary ion was also observed at *m/e* = 40, presumably C₂H₂N⁺. The hydride transfer reaction 11 is not probable because



it is endothermic by at least 65 kcal mol⁻¹.¹⁵ The only source

(15) The endothermicity of reaction 11 is based on a value for $\Delta H_{f,298}^\circ$ (CH₂Si⁺) of $227 \pm 7 \text{ kcal mol}^{-1}$ derived from the appearance potential of CH₂Si⁺ (with C₂H₆ and H₂) from trimethylsilane given by Hobrock and Kiser (Hobrock, B. G.; Kiser, R. W. *J. Phys. Chem.* **1962**, *66*, 155) and a value for $\Delta H_{f,298}^\circ$ (SiCH₃) of 77 kcal mol^{-1} given by Bell et al. (Bell, T. N.; Perkins, K. A.; Perkins, P. G. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1779). The formation of CH₂Si⁺ (and HCN) from the reaction of Si⁺ with acetonitrile leads to an upper limit of $283 \text{ kcal mol}^{-1}$ for $\Delta H_{f,298}^\circ$ (CH₂Si⁺) which is lower than the upper limit of $355 \text{ kcal mol}^{-1}$ based on the formation of this ion from the reaction of CH⁺ with silane reported previously by Stewart et al. (Stewart, G. W.; Henis, J. M. S.; Gaspar, P. P. *J. Chem. Phys.* **1972**, *57*, 1990).

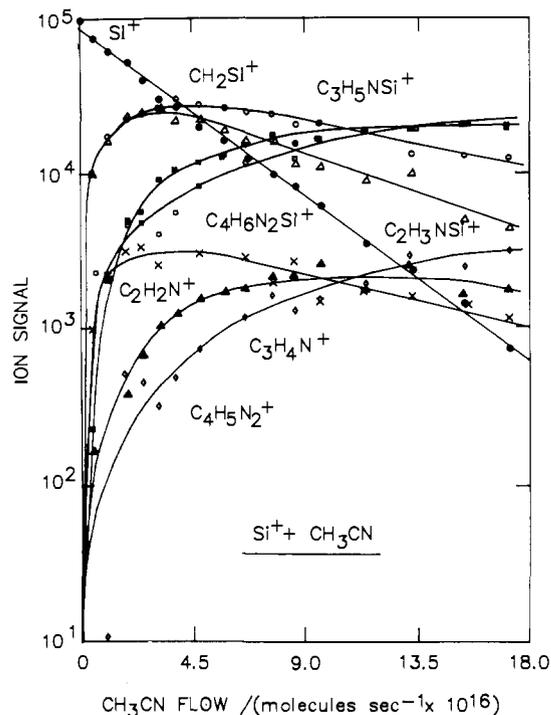


Figure 3. Observed variations in the ion signals recorded for the addition of acetonitrile into the reaction region of the SIFT apparatus in which Si⁺ is initially established as the dominant ion in helium buffer gas: *P* = 0.35 Torr, \bar{v} = $6.5 \times 10^3 \text{ cm s}^{-1}$, *L* = 46 cm, and *T* = 293 K.

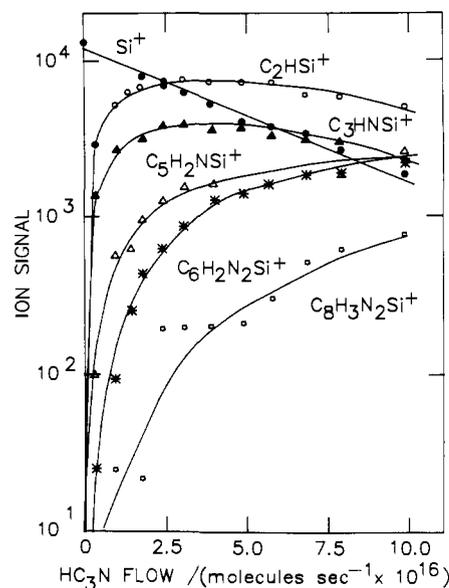


Figure 4. Observed variations in the ion signals recorded for the addition of cyanoacetylene into the reaction region of the SIFT apparatus in which Si⁺ is initially established as the dominant ion in helium buffer gas: *P* = 0.35 Torr, \bar{v} = $6.1 \times 10^3 \text{ cm s}^{-1}$, *L* = 46 cm, and *T* = 294 K.

of C₂H₂N⁺ appears to be the hydride transfer reaction 12. This conclusion is consistent with the observed product balance according to which the adduct C₄H₆N₂Si⁺ contributes only about 70% to the reactive decay of C₂H₃NSi⁺. The assignment of the *m/e* = 40 ion is further supported by the observed products indicated in Figure 3 as C₃H₄N⁺ and C₄H₅N₂⁺. CH₂CN⁺ is known to react with CH₃CN under SIFT conditions by adduct formation and elimination of HCN from the reaction intermediate as shown in reaction 13.¹⁶

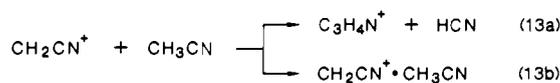
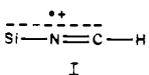
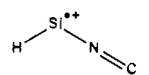
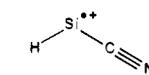
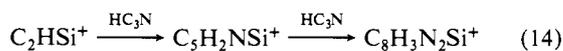


Table II. Computed Energies, Structural Parameters, and Charge Distributions for Three Isomers of CHNSi⁺

isomers	 I	 II	 III
total energy, ^a hartrees	-381.858421 (² Π)	-381.798854 (² A')	-381.793023 (² A')
relative energy, kcal mol ⁻¹	0.0	37.4	41.0
zero-point energy, kcal mol ⁻¹	12.2	9.40	8.93
bond lengths, Å	(Si-N) = 1.944 (N-C) = 1.133 (C-H) = 1.070	(Si-H) = 1.474 (Si-N) = 1.647 (N-C) = 1.188 ∠(HSiN) = 117.3	(Si-H) = 1.468 (Si-C) = 1.786 (C-N) = 1.147 ∠(HSiC) = 117.7
bond angles, deg			
charge distribution, electron charge units	Si: 0.7470 N: -0.5198 C: 0.3758 H: 0.3970	1.1140 -0.5493 0.4158 0.0195	1.0490 -0.0889 0.0042 0.0357

^aMP4 calculations were performed with the frozen-core approximation.

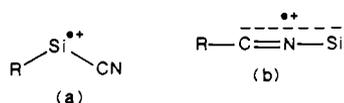
Cyanoacetylene. Cyanoacetylene was seen to react with Si⁺ at about 30% of the collision rate. The main product (70%) was C₂HSi⁺, but adduct formation was again observed to complete with the formation of bimolecular products. The higher order chemistry which was recorded is shown in Figure 4 and is consistent with the following clustering reactions:



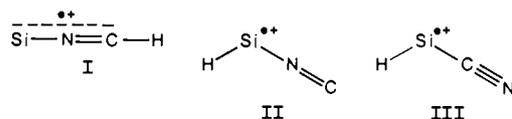
The addition of cyanoacetylene to the primary product ions C₂HSi⁺ and C₃HNSi⁺ was observed to proceed rapidly with effective bimolecular rate constants of $(1.1 \pm 0.5) \times 10^{-9}$ and $(1.3 \pm 0.5) \times 10^{-9}$ cm³ molecule⁻¹ s⁻¹, respectively.

Theoretical Results

At least two structures are possible for the adduct ions which were identified: those arising from C-C or C-H bond insertion as represented by (a) and those resulting from the formation of a Si-N bond with concomitant delocalization of an unpaired electron over the -CNSi moiety, as given in (b). To gain insight



into the relative stability of these structures calculations were performed at the MP4SDTQ/UHF/6-31G** level, with 6-31G** geometry-optimized structures, for the following three isomers of the simplest doublet system, CHNSi⁺:



The calculations were performed with the GAUSSIAN 82 program.¹⁷ The results are summarized in Table II which includes charge distributions based on a Mulliken population analysis. Table III lists spectral data which was also computed and which may be of use in future spectral searches in the laboratory or in extraterrestrial environments.

Discussion and Conclusions

The experimental results provide an instructive overview of the nature and degree of the reactivity of ground-state atomic silicon ions toward cyanide molecules of the type R-C≡N. The results

Table III. Harmonic Vibrational Frequencies (cm⁻¹), Rotational Constants A, B, and C (MHz), and Dipole Moments, μ (D), Computed at the UHF/6-31G** Level for Isomers of CHNSi⁺

	² Π (SiNCH ⁺)	² A' (HSiNC ⁺)	² A' (HSiCN ⁺)
	214 (π)	208 (a')	222 (a'')
	254 (π)	210 (a'')	240 (a')
	343 (σ)	775 (a')	710 (a')
	877 (π)	871 (a')	764 (a')
	970 (π)	2195 (a')	1926 (a')
	2321 (σ)	2318 (a')	2387 (a')
	3536 (σ)		
A		310093	314650
B	5107	6557	5627
C		6421	5528
μ	3.02	4.67	6.39

indicate that these are strongly dependent on the nature of R. For R = H, CH₃, and HC₂ the observed bimolecular products indicate elimination from the reaction intermediate of H, HCN, and CN, respectively. For R = CN elimination of CN occurs. A feature of the observed chemistry common to all four cyanides is the formation of an adduct ion, presumably by collisional stabilization of the reaction intermediate. The degree of stability of these open-shell adduct ions and their structure are uncertain.

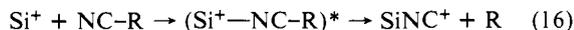
For the adduct ion formed in the reaction of Si⁺ with HCN, the computational results found in Table II show clearly that the linear ²Π species in which Si is bonded to N rather than C is energetically the most favorable structure of CHNSi⁺. The Si-N bond in this structure is relatively long and only partially covalent since only about 25% of the positive charge on Si is delocalized over the NCH moiety. The calculated Si⁺-NCH bond energy is 46.0 kcal mol⁻¹. (The corresponding data for the CNCH⁺ adduct ion calculated at the same level are 54% and 88.9 kcal mol⁻¹, respectively, with a C⁺-NCH bond length of 1.275 Å). Formation of structure II, although energetically allowed, is less probable because it requires the migration of the hydrogen atom from the carbon in structure I to the silicon prior to collisional stabilization. The insertion of Si⁺ into the H-C bond cannot compete significantly with Si-N bond formation since the resulting adduct ion is much less stable. However, the situation may be quite different for the formation of adduct ions between Si⁺ and the other cyanides since C-C bond insertion also becomes an option.

CNSi⁺ was observed to be the bimolecular product ion for the reactions of both HCN and C₂N₂ with Si⁺. The structural identity of this ion is questionable since two isomers, SiCN⁺ and CNSi⁺, are possible. Available thermochemical data indicates that the formation of the SiCN⁺ isomer from cyanogen is endothermic by at least 10 kcal mol⁻¹ and that its formation from hydrogen cyanide is at most 1 kcal mol⁻¹ exothermic when allowing for an uncertainty of ±19 kcal mol⁻¹ in the enthalpy of formation of SiCN⁺.¹⁸ MP4SDTQ/6-31G* calculations predict the SiNC⁺

(16) Wincel, H.; Wlodek, S.; Bohme, D. K. *Int. J. Mass Spectrom. In Processes* **1988**, *84*, 69.

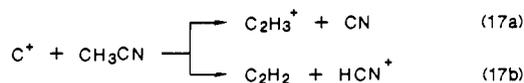
(17) Binkley, J. S.; Frish, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release A, Carnegie-Mellon University: Pittsburgh, PA.

isomer to be about 10.5 kcal mol⁻¹ more stable than the SiCN⁺ isomer.¹⁹ This result suggests that only the SiNC⁺ isomer is thermochemically allowed and so formed exclusively in the reaction of Si⁺ with cyanogen and possibly also in its reaction with HCN. The SiNC⁺ isomer will be formed if the Si⁺ approaches these two molecules end-on and attacks the N atom rather than insert into the C-C or C-H bonds as shown in reaction 16 where R = H,



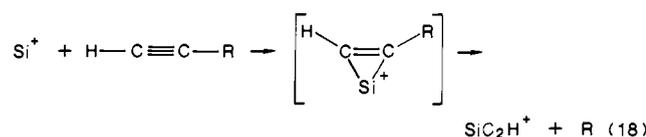
CN. It is interesting to note here that the production of SiNC⁺ from the reaction of Si⁺ with HCN is analogous to the production of CNC⁺ from the reaction of C⁺ with HCN. Available experimental evidence suggests that this latter reaction forms the CNC⁺ isomer exclusively.²⁰ Also, separate experiments in our laboratory have shown that C⁺ reacts with cyanogen to produce C₂N⁺, and available thermochemical information in this case indicates that only formation of the CNC⁺ isomer is exothermic.^{20,21}

C-C bond insertion becomes a possible competing mechanism for the reaction of Si⁺ with acetonitrile and can lead to the observed elimination of CHN, as can C-H bond insertion. The ionic product in both cases is likely to be H₂C=Si⁺. Attack at the N atom is unlikely to lead to CHN elimination but could contribute instead to the efficient formation of the adduct ion which may be H₃C-C⁺-N=Si. We are not aware of a previous published study of the analogous reaction of C⁺ with acetonitrile. Preliminary investigations in our laboratory indicate that this latter reaction results in the formation of bimolecular products which are quite different from the C analogues of the products observed with Si⁺. Two channels were observed for the reaction of C⁺ which are related by proton transfer. The differences in the observed



bimolecular products for the C⁺ and Si⁺ reactions are not surprising. The much higher enthalpy of formation of C⁺ (431 compared to 297 kcal mol⁻¹ for Si⁺) results in the fact that elimination of CN to form C₂H₃⁺ is quite exothermic for the C⁺ reaction (by 82 kcal mol⁻¹) but quite endothermic for the Si⁺ reaction leading to CN and SiCH₃⁺ (by 50 kcal mol⁻¹).

A comparison with the reaction of Si⁺ with acetylene is instructive in a discussion of the mechanism of the reaction of Si⁺ with cyanoacetylene. Under similar conditions of pressure and temperature these two reactions proceed in helium carrier gas with about the same efficiency and give the same kinds of products in about the same proportions.²² In both cases about 70% of the reaction branches into the formation of C₂HSi⁺ and 30% leads to the formation of the adduct ion. This implies that the H-C≡C- group in cyanoacetylene is subjected to Si⁺ attack rather than the -C≡N group. A possible mechanism would involve the following formation of a cyclic intermediate for R = H and CN.



HC₂Si⁺ is the analogue of C₃H⁺ which we have observed previously as the predominant product ion in the very rapid reaction

(18) The enthalpy of formation of SiCN⁺ at 298 K can be calculated to be 292.6 ± 18.5 kcal mol⁻¹ from the enthalpy of formation for SiCN, 92.0 ± 7 kcal mol⁻¹, and the ionization energy of SiCN, 8.7 ± 0.5 eV, given by Muenow et al. (Muenow, D. W.; Margrave, J. L. *J. Phys. Chem.* **1970**, *74*, 2577).

(19) Hopkinson, A. C.; Lien, M. H., unpublished results.

(20) Bohme, D. K.; Wjodek, S.; Raksit, A. B.; Schiff, H. I.; Mackay, G. I.; Keskinen, K. *J. Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 123.

(21) Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1985**, *63*, 217.

(22) Bohme, D. K.; Wjodek, S.; Fox, A. In *Rate Coefficients in Astrochemistry*; Millar, T. J., Williams, D. A., Eds.; Kluger Academic Press: 1988; p 193.

of C⁺ with cyanoacetylene.²³ Its observation as a product in the reaction of Si⁺ with cyanoacetylene implies an upper limit to the standard enthalpy of formation of SiC₂H⁺ of 274 kcal mol⁻¹. The silicon analogue, C₃NSi⁺, of the other product ion, C₄N⁺, observed for the reaction of C⁺ with cyanoacetylene was not observed to be formed in the reaction of Si⁺ with cyanoacetylene.

Overall, the most striking features which are apparent in the comparison of the laboratory reactions of Si⁺ and C⁺ are the following: 1. The reactions with C⁺ are uniformly faster and more efficient. The largest differences in efficiency occur with HCN and C₂N₂. The disparity in the efficiency, $k_{\text{exp}}/k_{\text{c}}$, decreases as follows (the efficiency for the reaction with Si⁺ is given first): HCN (0.0019 vs 0.73), C₂N₂ (0.13 vs 1.1), HC₃N (0.34 vs 1.1), and CH₃CN (0.53 vs 0.65). Also, with CH₃CN and HC₃N there are differences in the nature of the bimolecular products. 2. Under similar conditions of pressure and temperature, adduct formation is a competing channel in all of the reactions with Si⁺ but not in any of the analogous reactions with C⁺.

One attempt to rationalize these differences can be based on likely differences in the intermediate energy profiles for the reactions of Si⁺ and C⁺. If the potential energy profiles for these reactions can be described with a double minimum, as is the case with many other ion/molecule reactions,²⁴ the reaction rates will be dependent on the magnitude of the intermediate energy barrier and the overall reaction exothermicity which in turn are dependent on the type of reaction and the nature of the reactants and products. For *similar* reaction types, the more exothermic reactions are expected to have smaller intermediate energy barriers and therefore to be faster. A systematic trend within each family of reactions of C⁺ and Si⁺ is not expected because of a possible variation in the type of reaction due to variations in the position of attack and nature of the insertion. However, a correlation with exothermicity can be expected for reactions of C⁺ and Si⁺ with the *same neutral molecule*. The reactions of Si⁺ are known to be less exothermic than their carbon analogues with HCN and C₂N₂. The standard enthalpy changes for the reactions with HCN are +8 ± 19 and -24 kcal mol⁻¹ for Si⁺ and C⁺, respectively, and for the reactions with C₂N₂ they are +18 ± 19 and -14 kcal mol⁻¹, respectively. A similar situation is expected to apply with CH₃CN and HC₃N. A higher exothermicity for the reactions of C⁺ is consistent with the higher efficiencies and larger number of product channels observed for the reactions of C⁺.

If the bonding in the Si⁺ adducts is weaker and less covalent than the bonding in the C⁺ adducts, as our calculations of the bonding for the adducts of Si⁺ and C⁺ with HCN suggest, we can expect the first minimum in the intermediate energy profile to be shallower and the intermediate barrier leading to bond redistribution to be closer to the initial energy of the reactants for the reactions of Si⁺. This will make the conversion of the initial ion/molecule complex via the intermediate activated complex to the second ion/molecule complex less likely. In contrast, in the presence of third-body collisions, collisional stabilization to form the ion adduct can be expected to become more favorable.

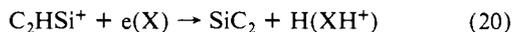
Reactions which result in the bonding of silicon to heteroatoms is of particular interest in the chemistry of partially ionized environments containing silicon, such as interstellar gas clouds, in connection with the formation and growth of silicon-containing molecules and small particles. Ion chemistry initiated by Si⁺ in these clouds can be followed by neutralization reactions and so lead to the formation of new molecules.²² For example, eventual neutralization of the product ion CNSi⁺ by charge transfer makes the reactions of Si⁺ with HCN and C₂N₂ possible sources for the CNSi molecule. (Given that CN and C₂ have similar electron affinities,¹⁴ it is interesting to note that the CNSi molecule may be largely ionic in character (CN⁻Si⁺) in analogy with the C₂Si⁺ electronic structure recently proposed for C₂Si.²⁵) The product CNSi⁺ ion may also play a role as a reactive intermediate in

(23) Raksit, A. B.; Bohme, D. K. *Can. J. Chem.* **1985**, *63*, 854.

(24) (a) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993. (b) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. (c) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *99*, 7891.

(25) Shepherd, R. A.; Graham, W. R. M. *J. Chem. Phys.* **1988**, *88*, 3399.

interstellar gas clouds in the manner proposed for the carbon analogue CNC^+ .²⁰ For example, CNC^+ reacts with molecules of the type HX in a manner similar to C^+ to lead to the formation of C-X bonds. Analogous reactions of CNSi^+ could lead to Si-X bond formation. The reactions of Si^+ with acetonitrile and cyanoacetylene are possible sources for SiCH and SiC_2 when followed by proton transfer or recombination with electrons as shown:

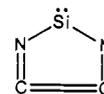


Homogeneous association reactions in interstellar gas clouds can proceed only by radiative association because of the low ambient gas densities. The association reactions of atomic Si^+ ions observed in the experiments reported here at moderate pressures of helium buffer gas are likely to be the result of intermolecular collisional stabilization of a relatively long-lived reaction intermediate. However, it should be noted that the contribution of bimolecular radiative association could not be evaluated since the total pressure of the ambient gas was not varied. In any case, all the association reactions observed with Si^+ were found to *compete* with bimolecular decomposition channels. In interstellar gas clouds radiative association which must compete with formation of bimolecular dissociation products can be argued to be unlikely.²⁶ On the other hand, the association reactions of silicon-containing molecular ions observed in our experiments which *do not compete* with bimolecular product

channels may well proceed by radiative association in interstellar gas clouds. When followed by neutralization of the adduct ions, these reactions could then provide sources for more complex molecules. A number of such possibilities are indicated by our experiments. The kinds of molecules that may be formed are quite intriguing, as shown, for example, in the following reaction sequences



where PT and e refer to neutralization by proton transfer and recombination with electrons, respectively. Here substituted silenes are the neutral molecules which may ultimately be produced. The five-membered ring molecule given below is even a possible product in reaction 21. However, the true nature of the neutral products



which may be formed in the final step in this chemistry is not known and remains to be explored and characterized.

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Registry No. Si^+ , 14067-07-3; HCN, 74-90-8; C_2N_2 , 460-19-5; CH_3CN , 75-05-8; HC_3N , 1070-71-9.

(26) Bates, D. R. *Astrophys. J.* **1983**, 267, L121.

Pressure Dependence of the Electronic Spectra of Quasi-One-Dimensional Pt_2X Semiconductors

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Abstract: The effects of high static pressure on the electronic absorption spectra of the mixed-valence semiconductors, $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{X}] \cdot 3\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$), have been investigated to 10.0 GPa. Their electronic spectra exhibit bands attributable to the reduced complex, $[\text{Bu}_4\text{N}]_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ ($d_{xz}, d_{yz} \rightarrow p\sigma$, $d\sigma^* \rightarrow d_{x^2-y^2}$, and $d\sigma^* \rightarrow p\sigma$), and the oxidized complex, $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{X}_2] \cdot 2\text{H}_2\text{O}$ ($d_{xz}, d_{yz} \rightarrow d\sigma^*$ and $\sigma(\text{X}) \rightarrow d\sigma^*$), along with an intervalence charge-transfer (IVCT) band characteristic of a mixed-valence solid. The reduced (Pt_2) and oxidized (Pt_2X_2) complexes have also been studied so that direct comparisons with the monohalides (Pt_2X) could be made. The $\sigma(\text{X}) \rightarrow d\sigma^*$ transition (observed at 34 500, 32 800, and 35 400 cm^{-1} for Pt_2Cl_2 , Pt_2Br , and Pt_2Cl , respectively) exhibits linear blue shifts of ca. 300 $\text{cm}^{-1}/\text{GPa}$ for each complex. The $d\sigma^* \rightarrow d_{x^2-y^2}$ transition in Pt_2 (35 300 cm^{-1}) shifts red initially and then begins to shift blue above 5.5 GPa, while the $d\sigma^* \rightarrow p\sigma$ band (ca. 27 000 cm^{-1}) exhibits little shift with pressure for Pt_2 , Pt_2Cl , and Pt_2Br . The dominant pressure-induced effects that give rise to the above shifts are (i) destabilization of the $d\sigma^*$ and $p\sigma$ levels through increased orbital overlap and d/p mixing and (ii) destabilization of the $d_{x^2-y^2}$ level at high pressure through increased ligand field interactions. The IVCT bands of Pt_2X exhibit strong red shifts with increasing pressure that are attributed to the movement of X in Pt_2X_2 toward Pt_2 in the linear chains that leads to an increase in the band character of the orbitals associated with this transition.

Quasi-one-dimensional, halide-bridged, mixed-valence, transition-metal complexes, MX , have been the focus of much recent research.²⁻⁸ An important characteristic of these materials is that their physical properties may be controlled by varying the transition metal complex ions, the halogen, and external pressure. The

materials exhibit an intense intervalence charge-transfer excitation, the IVCT band, that is polarized along the chain axis. Resonance

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