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# THE PROTON AFFINITY OF SiNH AND ITS FORMATION FROM $SiNH_2^+$ IN THE GAS PHASE

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$SiNH_2^+$ has been formed in the gas phase by the rapid reaction of $Si^+(^2P)$ with $NH_3$. Experimental and theoretical studies of the proton affinity of SiNH indicate that this ion is protonated at N, so that deprotonation produces selectively the isomer SiNH in partially ionized interstellar environments.

## 1. Introduction

Multiply bonded silicon analogues of carbon compounds are still rarely observed experimentally although there is an increasing interest in their properties and reactivity [1]. Hydrogen silaisonitrile, the silicon analogue of CNH, has been trapped in an argon matrix in an early study by Ogilvie and Cradock of the photolysis of silyl azide, $SiH_3N_3$, at 4 K [2]. However, to the best of our knowledge, SiNH has not yet been observed in the gas phase. Several interstellar emission lines have been tentatively attributed to free molecules of the isomer HSiN [3], but calculations are not consistent with this assignment. Quantum chemical studies of SiNH and its isomer, HSiN, indicate that HSiN is at least 55 kcal $mol^{-1}$ higher in energy than SiNH [4–7] and that the calculated microwave frequencies for HSiN do not match those which tentatively have been attributed to this molecule [5].

One possible source for SiNH in interstellar environments is the neutralization of $SiNH_2^+$ or isomeric $HSiNH^+$ by recombination with electrons or by proton transfer,

$$SiNH_2^+\ (HSiNH^+) + e\ (M) \rightarrow SiNH\ (HSiN) + H\ (MH^+)\ . \qquad (1)$$

Here we report results of an experimental study which indicates rapid reactions for the gas-phase formation of $SiNH_2^+$ from $Si^+(^2P)$ and ammonia and its subsequent neutralization by proton transfer. Limits to the proton affinity of SiNH are determined from the observation and failure to observe proton transfer with $SiNH_2^+$. Theoretical studies provide the proton affinity and heat of formation of SiNH and determine the preferred site of protonation.

## 2. Experimental

All measurements were performed with the selected ion flow tube apparatus described earlier [8,9]. Atomic $Si^+$ ions were generated by electron impact of $Si(CH_3)_4$ or $SiCl_4$ in a mixture with deuterium as described previously [10]. Deuterium was added to quench the excited $Si^+(^4P)$ state. The silicon ions were then selected and introduced into helium buffer gas at ≈0.35 Torr. One or two neutral reactants were added into the flow tube with inlets located in different positions. The purities of the reactant gases were as follows: $NH_3$ (Matheson, ⩾99.9%), $(CH_3)_2S$ (BDH, ⩾99%) and $(CH_3)_2CO$ (BDH, 99.5%). All experiments were made at 295±2 K.

## 3. Results and discussion

The reaction

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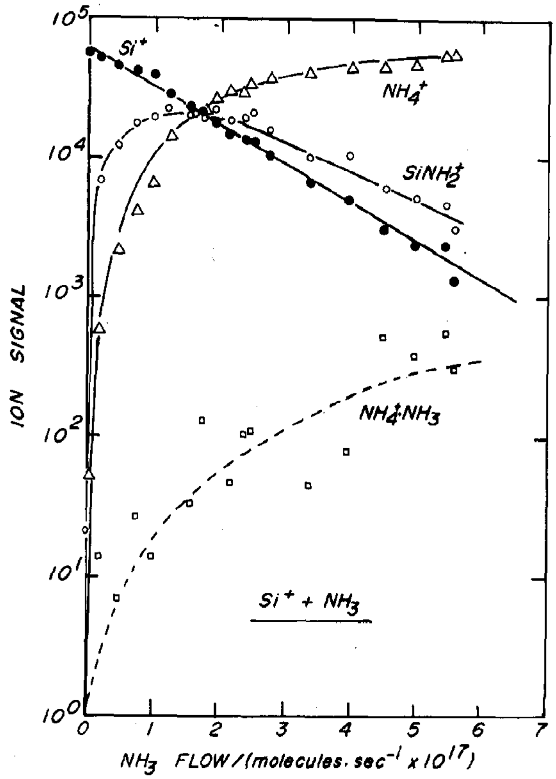

Fig. 1. Observations of the chemistry initiated by $Si^+$ in ammonia and helium buffer gas at a total pressure of 0.35 Torr. $T=295$ K, $\bar{v}=6.5\times10^3$ cm $s^{-1}$, and $L=46$ cm. The $Si^+$ is generated by electron impact at 71 eV in a 10 mol% mixture of $SiCl_4$ in deuterium which is added to remove the excited $Si(^4P)$ ions. The solid curves represent a computer fit assuming reactions (2) and (3) with $k_2=5.7\times10^{-10}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ and $k_3=7.4\times10^{-10}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ for this experiment. The dashed curve (drawn "by eye") describes the association reaction of $NH_4^+$ with ammonia.

$$Si^+ + NH_3 \rightarrow SiNH_2^+ + H \qquad (2)$$

was observed to occur rapidly when ammonia was introduced into the flow tube in which $Si^+(^2P)$ had been established as the dominant ion in helium buffer gas. The results are illustrated in fig. 1. The rate constant measured for reaction (2) was $6.4\times10^{-10}$ $cm^3$ molecule$^{-1}$ $s^{-1}$. The product ion, $SiNH_2^+$, which is thermalized by the predominant collisions with helium buffer gas atoms, reacted further with ammonia by proton transfer according to

$$SiNH_2^+ + NH_3 \rightarrow NH_4^+ + SiNH \qquad (3)$$

with a rate constant of $9.0\times10^{-10}$ $cm^3$ molecule$^{-1}$ $s^{-1}$ and a corresponding efficiency, $k/k_c$, of 0.4, where $k_c$ is the collision rate constant calculated according to the combined variational transition state theory -classical trajectory study of Su and Chesnavich [11]. The somewhat low reation efficiency suggests that reaction (3) is nearly isoergic or even slightly endoergic [12]and that the proton affinities of SiNH and $NH_3$ are close to each other. Indeed, further experiments with dimethyl sulfide and acetone, which have proton affinities only slightly below that of ammonia, indicate no proton transfer with $SiNH_2^+$. The reactions indicated in table 1 were observed instead. These results are consistent with a proton affinity for SiNH intermediate between the proton affinity of ammonia, 204.0 kcal $mol^{-1}$, and the proton affinity of dimethyl sulfide, 200.6 kcal $mol^{-1}$. The approximate empirical relationship between the efficiency of proton transfer and its standard free energy change suggests that the standard free energy change for reaction (3) is approximately equal to zero. The standard entropy change for reaction (3) was estimated from the changes in symmetry number according to

$$\Delta S^0 = R\ln\left(\frac{\sigma(SiNH_2^+)\,\sigma(NH_3)}{\sigma(NH_4^+)\,\sigma(SiNH)}\right). \qquad (4)$$

A value of $-2.2$ eu is obtained with the geometries calculated for $SiNH_2^+$ and SiNH (see below). The standard enthalpy change is then $\approx -0.6$ kcal $mol^{-1}$ so that $PA(SiNH) \approx PA(NH_3) - 0.6$ kcal $mol^{-1} =$ 203.4 kcal $mol^{-1}$. Finally, accounting for experimental uncertainties, we conclude that PA(SiNH) $=203\pm2$ kcal $mol^{-1}$.

There has been no previous determination, either experimental or theoretical, of the proton affinity of SiNH. In this study we have calculated the proton affinity of SiNH at the MP4SDTQ/6-31G** level for protonation at either the silicon or the nitrogen atom. Geometry optimizations were performed using the MONSTERGAUSS program [14] and MP4 calculations [15] were obtained with the GAUSSIAN 82 program [16]. We optimized the geometries of neutral SiNH and the two protonated isomers $HSiNH^+$ and $SiNH_2^+$ using standard 6-31G** basis sets [17,18] The total electron energies were corrected for electron correlation using MP4SDTQ/6-31G**. The computational results are summarized in table 2. The energy of $-344.199309$ au obtained for SiNH

Table 1
Rate constants (in units of $10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and product distributions at 295±2 K obtained for reactions of $SiNH_2^+$ with molecules B [a]

| B | PA [b] (kcal mol$^{-1}$) | Products | Product distribution | $k$ | $k/k_c$ [c] |
|---|---|---|---|---|---|
| $(CH_3)_2CO$ | 196.7 | $CH_4NSi^+ + (C_2H_4O)$ | 0.85 | 2.4 | 0.81 |
| | | $SiNH_2^+ \cdot (CH_3)_2CO$ | 0.15 | | |
| $(CH_3)_2S$ | 200.6 | $CH_2SCH_3^+ + (SiNH_3)$ | 0.70 | 1.5 | 0.70 |
| | | $SiNH_2^+ \cdot (CH_3)_2S$ | 0.25 | | |
| | | $CH_4NSi^+ + CH_3SH$ | 0.05 | | |
| $NH_3$ | 204.0 | $NH_4^+ + SiNH$ | 1.0 | 0.90 | 0.40 |

[a] All primary product ions which contribute 5% or more are listed. The product distributions have been rounded off to the nearest 5% and are estimated to be accurate to ±30%. The accuracy of the rate constants is estimated to be better than ±30%. The values for the rate constants are averages for at least three measurements.

[b] Proton affinities were taken from the compilation in ref. [13].

[c] The collision rate constants $k$ have been calculated according to the combined variational transition state theory–classical trajectory study described in ref. [11].

may be compared with the value of −344.18931 au calculated by Luke et al. [6] at MP4SDTQ/6-31G*//321G* level, and the value of −344.210448 au calculated by Kroto et al. [5] with a CI treatment using a high quality basis set. The proton affinities of SiNH were calculated using

$$SiNH + H^+ \rightarrow SiNH_2^+ \ (HSiNH^+)\,, \qquad (5)$$

$$PA(SiNH) = -\Delta E_e^0 - \Delta E_v^0 - \Delta(\Delta E_v^{298}) - \Delta E_r^{298} + \tfrac{5}{2}RT\,, \qquad (6)$$

where $\Delta E_e^0$ is the change in electronic energy for process (5), $\Delta E_v^0$ is the zero-point vibrational energy difference, and $\Delta E_v^{298}$ and $\Delta E_r^{298}$ correspond to the vibrational and rotational energy differences, respectively, at room temperature. The calculated proton affinities are 202.8 kcal mol$^{-1}$ for protonation at N and 149.4 kcal mol$^{-1}$ for protonation at Si.

The good agreement between the experimental value of the proton affinity and that calculated for protonation at nitrogen establishes that $SiNH_2^+$ is the isomer produced in reaction (2). The calculated net atomic charges for $SiNH_2^+$ are Si, +1.047; N,

Table 2
SCF and MP4SDTQ/6-31G** energies and geometries for SiNH, $SiNH_2^+$ and $HSiNH^+$

| Species | Symmetry | State | Geometry [a] | $E_{SCF}$ (au) | $E_v^0$ [b] ($E_v^{298}$) | $E_{MP4}$ (au) |
|---|---|---|---|---|---|---|
| SiNH | $C_{\infty v}$ | $^1\Sigma^+$ | (SiN) = 1.527<br>(NH) = 0.987 | −343.92268 | 9.53<br>(9.72) | −344.19931 |
| $SiNH_2^+$ | $C_{2v}$ | $^1A_1$ | (NH) = 1.008<br>(SiN) = 1.644<br>∠(SiNH) = 124.7<br>∠(HNH) = 110.7 | −344.26966 | 16.58<br>(16.74) | −344.53182 |
| $HSiNH^+$ | $C_{\infty v}$ | $^1\Sigma^+$ | (HSi) = 1.449<br>(SiN) = 1.481<br>(NH) = 0.993 | −344.16558 | 13.94<br>(14.30) | −344.44285 |

[a] All bond lengths are in Å and bond angles in deg.

[b] Zero-point energy ($E_v^0$) and vibrational energy at room temperature ($E_v^{298}$) in kcal mol$^{-1}$ based on frequencies obtained at the SCF level.

$-0.824$, and H, $+0.388$. The largest contribution to the HOMO of this species is the 3s atomic orbital of silicon so that the structure of $SiNH_2^+$ may be described as the silene $:Si^+-NH_2$.

The ionic products which were observed for the reactions of $SiNH_2^+$ with $(CH_3)_2CO$ and $(CH_3)_2S$ are consistent with a silene character for $SiNH_2^+$ since they can be formed by carbene-like insertion into C–C and C–S bonds or, in the case of $(CH_3)_2S$, by $H^-$ transfer to form the aminosilylene $:Si(H)NH_2$ which has been calculated to be approximately 18 kcal mol$^{-1}$ more stable than the silanimine isomer $H_2SiNH$ [19].

The high rate constants for reactions (2) and (3) suggest that SiNH is an important interstellar molecule in regions rich in ammonia. Its detection, however, is likely to be a difficult task since SiNH has only a small dipole moment. Our calculated value at the SCF/6-31G** level is only 0.16 D, which can be compared to the values of 0.26 D calculated by Luke et al. [6] and 0.20 D calculated by Roelandt et al. [7].

Finally, the heat of formation of SiNH was estimated from quantum chemical calculations of the enthalpy change for the process

$$SiNH(^1\Sigma^+)\rightarrow Si(^3P)+NH(^3\Sigma^-)\,, \qquad (7)$$

which has a value of 137.7 kcal mol$^{-1}$ at the MP4/6-31G**//6-31G** level. This leads to a standard heat of formation for SiNH, $\Delta H^0_{f,298}(SiNH)=50.2$ kcal mol$^{-1}$, when combined with $\Delta H^0_{f,298}(Si)=108.9$ kcal mol$^{-1}$ and $\Delta H^0_{f,298}(NH)=79$ kcal mol$^{-1}$ [20]. Knowledge of the standard heat of formation of SiNH, the proton affinities of SiNH, and the heat of formation of the proton, results in standard heats of formation of the ions $SiNH_2^+$ and $HSiNH^+$ of 214.2 and 267.8 kcal mol$^{-1}$ at 298 K. These latter results lead to the conclusion that reaction (2) is exothermic by 17.3 kcal mol$^{-1}$ for the formation of the $SiNH_2^+$ isomer and endothermic by 36.3 kcal mol$^{-1}$ for the formation of the $HSiNH^+$ isomer.

Further studies are now in progress of other reactions which lead to the formation or depletion of $SiNH_2^+$ and which involve $SiNH_2^+$ in still further evolution of higher-order silicon compounds.

## 4. Conclusions

Ionized atomic silicon has been observed to react rapidly with ammonia at 295 ± 2 K to produce hydrogen silaisonitrile protonated at nitrogen. The identity of the product ion has been established through experimental and theoretical examinations of the proton product affinity of hydrogen silaisonitrile. Free neutral molecules of silaisonitrile can be produced when this reaction is followed by deprotonation as is likely, for example, in partially ionized interstellar environments containing ammonia.

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