**Supporting Information**

**Directed Gas-Phase Formation of Aminosilylene (HSiNH2; X1A') - the Simplest Silicon Analogue of an Aminocarbene - under Single-Collision Conditions**

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Considering the existence of ground state atomic silicon (Si; 3Pj) in our primary beam, the crossed molecular beam experiments of silicon with ammonia (NH3; X1A1) and D3-ammonia (ND3; X1A1) were also conducted to gauge potential interferences and reactive scattering signal. Atomic silicon was prepared through ablation of a rotating silicon rod with 266 nm laser pulse (5 ± 1 mJ per pulse; 30 Hz) and neon gas (Ne; 99.999%; Matheson) was released by a pulsed piezoelectric valve operated at a backing pressure of 4 atm and a repetition rate of 60 Hz. No signal at m/z = 43 in the Si (28 amu) - NH3 (17 amu) system or at m/z = 46 in the Si (28 amu) - ND3 (20 amu) system was detected, indicating that both H2 loss and D loss pathway were closed in the Si – NH3/ND3 systems. These experimental results agree well with the Si-NH3 potential energy surface (PES).[1](#_ENREF_1) Theoretical calculations indicate that Si+NH3 reaction start with the barrierless adduction leading to the formation of SiNH3 complex on both the singlet and triplet PES, but the followed isomerization from SiNH3 to HSiNH2 intermediates on the singlet and triplet PES are closed by the insurmountable transition states located about 26 kJ mol-1 and 65 kJ mol-1 above the separated reactant (Si, 3Pj; NH3; X1A1), respectively. It is clear that no signal is detectable in Si-NH3/ND3 systems, we can then conclude all the scattering signal under our experimental condition (SiD beam) should come from SiD - NH3/ND3 systems, namely no interference from Si radicals in the primary beam.

![图示

描述已自动生成]()

**Figure S1.** Potential energy surface for the reaction of the silylidyne radical (SiH) with ammonia (NH3). Colors of the atoms: silicon, purple; nitrogen, blue and hydrogen, white.

**Table S1.** Peak Velocity (vp) and Speed Ratios (S) of the D1-Silylidyne (SiD), Ammonia (NH3) and Ammonia-d3 (ND3) Beams along with the Corresponding Collision Energy (EC) and Center-of-Mass Angle () for each reactive scattering experiment. The speed ratio is defined as as 1.65/(Δν/ν) with the peak velocity of the beam (ν) and the corresponding velocity spread (Δν).[2](#_ENREF_2)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| beam | vp (m s-1) | S | Ec (kJ mol-1) | (deg) |
| SiD (X2Π) | 1202 ± 26 | 6.1 ± 1.1 |  |  |
| NH3 (X1A1) | 1143 ± 34 | 10.3 ± 1.4 | 14.9 ± 0.4 | 28.3 ± 0.4 |
| SiD (X2Π) | 1206 ± 25 | 6.2 ± 1.2 |  |  |
| ND3 (X1A1) | 1091 ± 25 | 10.1 ± 1.3 | 15.9 ± 0.4 | 31.2 ± 0.5 |

**Table S2**. Optimized Cartesian coordinates (Å), and vibrational frequencies (cm-1) of reactants, selected products, intermediates, transition states involved in the silylidyne radical (SiH) plus ammonia(NH3) reaction.

|  |  |  |
| --- | --- | --- |
| Species | Vibrational Frequencies (cm-1) | Cartesian Coordinates (Å)  Atom X Y Z |
| **Ammonia** | 1072.0 1681.9 1682.0  3460.5 3579.3 3579.5 | 7 0.000006 0.000000 -0.115882  1 -0.451902 0.823641 0.270386  1 -0.487366 -0.803165 0.270386  1 0.939227 -0.020475 0.270403 |
| **Silylidyne** | 2072.67 | 14 0.000000 0.000000 0.101986  1 0.000000 0.000000 -1.427802 |
| **i1** | 177.6 359.7 541.7  570.8 867.6 1247.7  1659.9 1661.8 1965.1  3460.5 3563.1 3577.2 | 7 -1.226538 -0.006065 -0.000037  1 -1.627568 -0.939910 0.000099  1 -1.571553 0.484070 0.821826  1 -1.572351 0.484271 -0.821441  14 0.893832 -0.101619 -0.000018  1 0.843586 1.436688 0.000030 |
| **i2** | 204.6 430.8 645.6  752.7 819.3 902.7  905.4 1596.1 2139.8  2175.4 3570.3 3659.9 | 7 1.104269 -0.000054 0.088726  14 -0.623778 -0.000032 -0.111352  1 1.643749 -0.831642 -0.105749  1 1.643002 0.832188 -0.105137  1 -1.141795 1.223891 0.574106  1 -1.141951 -1.223606 0.574623 |
| **i3** | 106.1 555.1 635.8  746.5 874.8 924.0  939.3 985.0 2187.5  2196.4 2253.9 3447.3 | 7 1.235385 0.142435 -0.007838  14 -0.520249 -0.008863 -0.002611  1 1.723160 -0.758449 -0.020960  1 -0.926014 -0.265837 1.409624  1 -1.050573 -1.120040 -0.842852  1 -1.110782 1.271368 -0.454396 |
| **i1– i2** | 1589.1*i* 504.4 618.2  644.8 709.3 925.2  1001.1 1563.4 1715.8  2098.4 3559.0 3680.4 | 7 -1.137082 0.018258 -0.059332  1 -1.710795 -0.810631 -0.149699  1 -1.680474 0.873425 -0.061401  1 -0.410636 -0.208245 1.115771  14 0.778090 -0.099411 -0.040803  1 0.868214 1.409403 0.081898 |
| **i1 – p2** | 1396.6*i* 274.0 341.8  507.3 705.1 854.6  867.3 918.9 1299.2  1906.4 1928.3 3586.9 | 7 0.857052 0.312216 0.000000  1 1.798722 -0.612428 0.000000  1 1.398242 1.167852 0.000000  1 2.484833 -1.183882 0.000000  14 -0.745702 -0.201119 0.000000  1 -1.241328 1.258613 0.000000 |
| **i1 – p1** | 1400.3*i* 327.4 552.4  643.8 742.0 957.6  1271.9 1552.9 1777.1  1916.5 3524.8 3618.0 | 7 1.125613 -0.035705 0.000000  1 1.636408 -0.301217 -0.832726  1 0.402055 1.202846 0.000000  1 1.636469 -0.299819 0.833107  14 -0.791263 -0.139259 0.000000  1 -0.476541 1.597753 0.000000 |
| **i2 – i3** | 1774.5*i* 502.6 604.3  702.3 765.5 870.7  943.2 1002.1 1925.5  2176.0 2250.6 3464.7 | 7 1.168758 0.119449 -0.142244  14 -0.555422 -0.013736 0.038636  1 0.525531 0.159770 1.182431  1 1.659783 -0.771372 -0.032976  1 -1.324079 -1.243828 -0.306929  1 -1.266637 1.211586 -0.387718 |
| **i2 – p1** | 694.6*i* 389.3 497.9  574.9 687.8 772.1  864.5 1430.7 1599.7  1630.8 3554.8 3651.1 | 7 -1.091504 0.032568 0.022427  14 0.652413 -0.200029 -0.018567  1 -1.596638 0.898210 -0.108756  1 -1.716624 -0.760997 0.058263  1 0.998248 1.147178 0.800204  1 0.821759 1.288035 -0.646768 |
| **i3 – p2** | 1305.0*i* 392.0 520.0  599.9 645.8 797.6  962.6 1009.8 1244.3  1949.7 2305.0 3592.0 | 7 1.183107 0.041899 0.099998  14 -0.432414 0.103530 -0.112888  1 1.759781 -0.758920 -0.130733  1 -1.195334 1.202413 0.495328  1 -1.367216 -1.089937 0.789547  1 -1.425187 -1.096269 -0.273696 |
| **p1**, SiNH2 | 597.6 745.7 853.2  1589.8 3508.2 3587.7 | 7 0.996286 -0.000001 0.000000  14 -0.722563 -0.000001 0.000000  1 1.570926 0.835230 0.000000  1 1.570951 -0.835215 0.000000 |
| **p2**, HSiNH | 523.5 619.3 713.1  1065.7 1998.9 3643.1 | 7 0.032276 1.038345 0.000000  14 0.032276 -0.570073 0.000000  1 0.730038 1.768454 0.000000  1 -1.407844 -1.055840 0.000000 |
| **p3**, HSiNH2 | 603.0 701.5 753.2  855.8 973.5 1604.7  1995.7 3553.2 3645.8 | 7 1.034403 0.016756 0.000000  14 -0.681201 -0.113704 0.000000  1 1.629077 -0.800790 0.000000  1 1.573940 0.871699 0.000000  1 -0.907028 1.403655 0.000000 |
| **p4,** H2SiNH | 586.9         607.7       746.5  771.7        1003.3     1128.2  2195.5      2287.8     3586.2 | 14          -0.488865    0.014605   0.000000  7             1.106242   -0.127318    0.000000  1            -1.339191    1.236586    0.000000  1           -1.283610   -1.226996   0.000000  1             1.723219    0.677171   0.000000 |

**References**

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