Supporting Information

Directed Gas-Phase Formation of Aminosilylene ($HSiNH_2$; X^1A') - the Simplest Silicon Analogue of an Aminocarbene - under Single-Collision Conditions

Zhenghai Yang, Chao He, Shane Goettl, Ralf I. Kaiser*

Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, USA

Corresponding Author Prof. Dr. Ralf I. Kaiser: ralfk@hawaii.edu

Valeriy N. Azyazov

Lebedev Physical Institute, Samara 443011, Russian Federation

Alexander M. Mebel*

Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

Corresponding Author Prof. Dr. Alexander M. Mebel: mebela@fiu.edu

Considering the existence of ground state atomic silicon (Si; ^3P_j) in our primary beam, the crossed molecular beam experiments of silicon with ammonia (NH_3; X^1A_1) and D3-ammonia (ND_3; X^1A_1) 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) - NH_3 (17 amu) system or at m/z = 46 in the Si (28 amu) - ND_3 (20 amu) system was detected, indicating that both H_2 loss and D loss pathway were closed in the Si – NH_3/ND_3 systems. These experimental results agree well with the Si-NH_3 potential energy surface (PES).[1] Theoretical calculations indicate that Si+NH_3 reaction start with the barrierless adduction leading to the formation of $SiNH_3$ complex on both the singlet and triplet PES, but the followed isomerization from $SiNH_3$ to $HSiNH_2$ 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, ^3P_j; NH_3; X^1A_1), respectively. It is clear that no signal is detectable in Si-NH_3/ND_3 systems, we can then conclude all the scattering signal under our experimental condition (SiD beam) should come from SiD - NH_3/ND_3 systems, namely no interference from Si radicals in the primary beam.

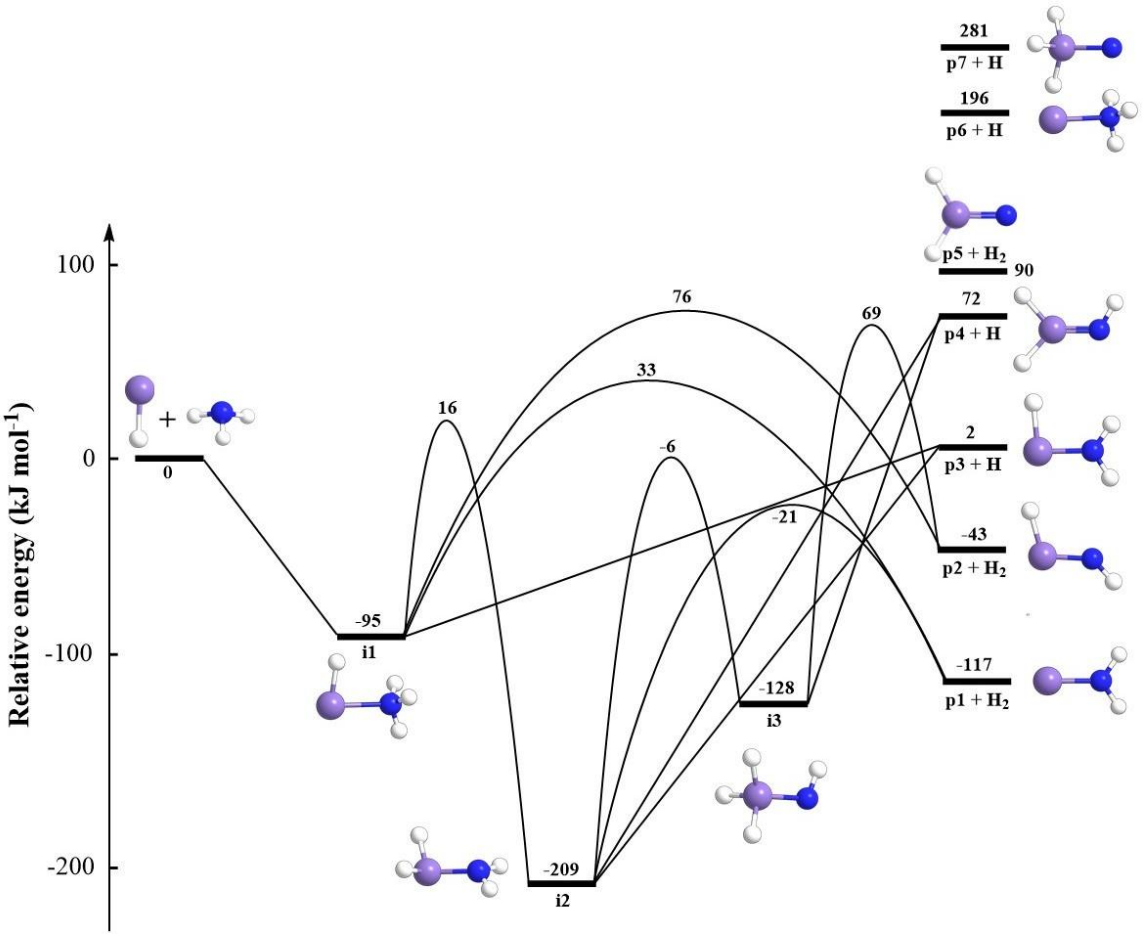

Figure S1. Potential energy surface for the reaction of the silylidyne radical (SiH) with ammonia (NH_3). Colors of the atoms: silicon, purple; nitrogen, blue and hydrogen, white.

Table S1. Peak Velocity (v_p) and Speed Ratios (S) of the D1-Silylidyne (SiD), Ammonia (NH_3) and Ammonia-d3 (ND_3) Beams along with the Corresponding Collision Energy (E_C) and Center-of-Mass Angle (Θ_{CM}) for each reactive scattering experiment. The speed ratio is defined as as $1.65/(\Delta v/v)$ with the peak velocity of the beam (v) and the corresponding velocity spread (Δv).[2]

beam	v_p (m s^{-1})	S	E_c (kJ mol^{-1})	Θ_{CM} (deg)
SiD ($X^2\Pi$)	1202 ± 26	6.1 ± 1.1		
NH_3 (X^1A_1)	1143 ± 34	10.3 ± 1.4	14.9 ± 0.4	28.3 ± 0.4
SiD ($X^2\Pi$)	1206 ± 25	6.2 ± 1.2		
ND_3 (X^1A_1)	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 (NH_3) reaction.

Species	Vibrational Frequencies (cm^{-1})	Cartesian Coordinates (Å)			
		Atom	X	Y	Z
Ammonia	1072.0 1681.9 1682.0	7	0.000006	0.000000	-0.115882
	3460.5 3579.3 3579.5	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	7	-1.226538	-0.006065	-0.000037
	570.8 867.6 1247.7	1	-1.627568	-0.939910	0.000099
	1659.9 1661.8 1965.1	1	-1.571553	0.484070	0.821826
	3460.5 3563.1 3577.2	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	7	1.104269	-0.000054	0.088726
	752.7 819.3 902.7	14	-0.623778	-0.000032	-0.111352
	905.4 1596.1 2139.8	1	1.643749	-0.831642	-0.105749
	2175.4 3570.3 3659.9	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	7	1.235385	0.142435	-0.007838
	746.5 874.8 924.0	14	-0.520249	-0.008863	-0.002611
	939.3 985.0 2187.5	1	1.723160	-0.758449	-0.020960
	2196.4 2253.9 3447.3	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	7	-1.137082	0.018258	-0.059332
	644.8 709.3 925.2	1	-1.710795	-0.810631	-0.149699
	1001.1 1563.4 1715.8	1	-1.680474	0.873425	-0.061401
	2098.4 3559.0 3680.4	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	7	0.857052	0.312216	0.000000
	507.3 705.1 854.6	1	1.798722	-0.612428	0.000000
	867.3 918.9 1299.2	1	1.398242	1.167852	0.000000
	1906.4 1928.3 3586.9	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	7	1.125613	-0.035705	0.000000

	643.8	742.0	957.6	1	1.636408	-0.301217	-0.832726
	1271.9	1552.9	1777.1	1	0.402055	1.202846	0.000000
	1916.5	3524.8	3618.0	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	7	1.168758	0.119449	-0.142244
	702.3	765.5	870.7	14	-0.555422	-0.013736	0.038636
	943.2	1002.1	1925.5	1	0.525531	0.159770	1.182431
	2176.0	2250.6	3464.7	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	7	-1.091504	0.032568	0.022427
	574.9	687.8	772.1	14	0.652413	-0.200029	-0.018567
	864.5	1430.7	1599.7	1	-1.596638	0.898210	-0.108756
	1630.8	3554.8	3651.1	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	7	1.183107	0.041899	0.099998
	599.9	645.8	797.6	14	-0.432414	0.103530	-0.112888
	962.6	1009.8	1244.3	1	1.759781	-0.758920	-0.130733
	1949.7	2305.0	3592.0	1	-1.195334	1.202413	0.495328
				1	-1.367216	-1.089937	0.789547
				1	-1.425187	-1.096269	-0.273696
p1, $SiNH_2$	597.6	745.7	853.2	7	0.996286	-0.000001	0.000000
	1589.8	3508.2	3587.7	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	7	0.032276	1.038345	0.000000
	1065.7	1998.9	3643.1	14	0.032276	-0.570073	0.000000
				1	0.730038	1.768454	0.000000
				1	-1.407844	-1.055840	0.000000
p3, $HSiNH_2$	603.0	701.5	753.2	7	1.034403	0.016756	0.000000
	855.8	973.5	1604.7	14	-0.681201	-0.113704	0.000000
	1995.7	3553.2	3645.8	1	1.629077	-0.800790	0.000000
				1	1.573940	0.871699	0.000000
				1	-0.907028	1.403655	0.000000
p4, H_2SiNH	586.9	607.7	746.5	14	-0.488865	0.014605	0.000000
	771.7	1003.3	1128.2	7	1.106242	-0.127318	0.000000
	2195.5	2287.8	3586.2	1	-1.339191	1.236586	0.000000
				1	-1.283610	-1.226996	0.000000
				1	1.723219	0.677171	0.000000

References

(1) Chen, M.; Zheng, A.; Lu, H.; Zhou, M. Reactions of Atomic Silicon and Germanium with Ammonia: A Matrix-Isolation FTIR and Theoretical Study. *J. Phys. Chem. A* **2002**, *106*, 3077-3083.

(2) Buckland, J. R.; Folkerts, R. L.; Balsod, R. B.; Allison, W. A Simple Nozzle Design for High Speed-Ratio Molecular Beams. *Meas. Sci. Technol.* **1997**, *8*, 933.