

## Supporting Information

### Gas-Phase Preparation of Silyl Cyanide ( $\text{SiH}_3\text{CN}$ ) via a Radical Substitution Mechanism

Zhenghai Yang<sup>a</sup>, Chao He<sup>a</sup>, Shane J. Goettl<sup>a</sup>, Dababrata Paul<sup>a</sup>, Ralf I. Kaiser<sup>a\*</sup>,  
Mateus X. Silva<sup>b</sup>, Breno R. L. Galvão<sup>b\*</sup>

<sup>a</sup>*Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, USA*

<sup>b</sup>*Centro Federal de Educação Tecnológica de Minas Gerais, CEFET-MG, Av. Amazonas  
5253, 30421-169 Belo Horizonte, Minas Gerais, Brazil*

\*Email: [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu); [brenogalvao@gmail.com](mailto:brenogalvao@gmail.com)

**Table S1.** Peak velocities ( $v_p$ ) and speed ratios (S) of the cyano (CN), and silane ( $\text{SiH}_4$ ) beams along with the corresponding collision energy ( $E_c$ ) and center-of-mass angle ( $\theta_{\text{CM}}$ ).

| Beam           | $v_p$ (m s <sup>-1</sup> ) | S          | $E_c$ (kJ mol <sup>-1</sup> ) | $\theta_{\text{CM}}$ (deg) |
|----------------|----------------------------|------------|-------------------------------|----------------------------|
| CN             | 1350 ± 24                  | 3.7 ± 0.2  |                               |                            |
| $\text{SiH}_4$ | 827 ± 20                   | 10.1 ± 0.2 | 18.2 ± 0.5                    | 37.0 ± 0.5                 |

**Table S2.** Results of our methodology and experimental results for prototypical carbon, and silicon molecules, including the CN radical.

| Reaction  | Calculated (kJ mol <sup>-1</sup> ) | Exp. (kJ mol <sup>-1</sup> )                 |
|---|------------------------------------|--|
| $\text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}$                  | 379                                | 378 <sup>1</sup>                             |
| $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$                    | 432                                | 432.273 ± 0.065 <sup>2</sup>                 |
| $\text{CN} \rightarrow \text{C}(^3\text{P}) + \text{N}(^4\text{S})$ | 736                                | 750 ± 5 <sup>3</sup><br>747 ± 2 <sup>4</sup> |

**Table S3.** Optimized Cartesian coordinates (Å), and vibrational frequencies (cm<sup>-1</sup>) of reactants, products, intermediates, and transition states involved in the cyano radical (CN) plus silane (SiH<sub>4</sub>) reaction.

REACTANTS

CN

|   |          |          |           |
|---|----------|----------|-----------|
| C | 0.000000 | 0.000000 | -0.630897 |
| N | 0.000000 | 0.000000 | 0.542494  |

Frequencies

2081.18

SiH<sub>4</sub>

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | -0.000013 | -0.000000 | 0.000003  |
| H  | -0.000010 | -0.000000 | 1.476002  |
| H  | 1.391571  | 0.000000  | -0.492009 |
| H  | -0.695773 | -1.205168 | -0.491995 |
| H  | -0.695773 | 1.205168  | -0.491995 |

Frequencies Frequencies

938.08

939.63

941.24

993.49

994.60

2263.75

2268.98

2269.06

2269.20

PRODUCTS

HCN

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.000000 | -0.000000 | -0.556661 |
| N | 0.000000  | 0.000000  | 0.597399  |
| H | 0.000000  | 0.000000  | -1.620517 |

Frequencies

749.46

749.48

2128.21

3466.92

HNC

|   |           |           |           |
|---|-----------|-----------|-----------|
| N | -0.000000 | -0.000000 | -0.482678 |
| C | 0.000000  | 0.000000  | 0.686734  |
| H | 0.000000  | 0.000000  | -1.478019 |

Frequencies

488.17

488.21

2064.34

3827.57

SiH<sub>3</sub>

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 0.000690  | 0.042387  | 0.002157  |
| H  | 1.286250  | -0.407464 | 0.576029  |
| H  | -1.136063 | -0.408913 | 0.831853  |
| H  | -0.146221 | -0.414000 | -1.395749 |

Frequencies

790.74

953.54

956.91

2226.52

2261.27

2261.83

SiH<sub>3</sub>CN

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 0.008463  | -0.014512 | 0.005842  |
| H  | -0.015306 | 0.026422  | 1.475201  |
| H  | 1.385991  | 0.026227  | -0.506029 |
| H  | -0.715769 | -1.186880 | -0.506292 |
| C  | -0.863932 | 1.496800  | -0.611183 |
| N  | -1.411649 | 2.444362  | -0.997534 |

Frequencies

273.52

277.06

601.62

705.18

706.16

945.88

968.45

969.17

2234.18

2287.62

2300.93

2301.72

SiH<sub>3</sub>NC

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | -0.007272 | 0.012668  | -0.005219 |
| H  | -0.030662 | 0.053087  | 1.463062  |
| H  | 1.369374  | 0.052639  | -0.516387 |
| H  | -0.730505 | -1.159323 | -0.516486 |
| N  | -0.828635 | 1.436055  | -0.586526 |
| C  | -1.384501 | 2.397293  | -0.978439 |

Frequencies

192.92

193.44

672.98

721.72

722.28

969.65

971.91  
972.14  
2131.58  
2296.48  
2305.22  
2305.35

INTERMEDIATES

**vdW1:** H<sub>4</sub>Si--NC

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 0.000595  | 0.000151  | -1.842504 |
| H  | 1.379033  | 0.202210  | -1.357443 |
| H  | -0.514738 | -1.296159 | -1.362629 |
| H  | -0.865604 | 1.092915  | -1.361036 |
| H  | 0.003598  | 0.001600  | -3.320691 |
| N  | 0.000309  | 0.000111  | 1.476325  |
| C  | 0.000341  | 0.000118  | 2.648662  |

Frequencies

63.14  
84.86  
84.87  
213.35  
213.82  
931.58  
940.43  
940.52  
993.34  
993.41  
2086.66  
2254.00  
2267.22  
2271.37  
2271.52

**vdW2:** H<sub>3</sub>SiH--NC

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 2.282587  | 0.005383  | 0.014599  |
| H  | 2.772252  | 1.314211  | 0.491534  |
| H  | 2.778659  | -1.057388 | 0.911622  |
| H  | 2.787031  | -0.235408 | -1.352109 |
| H  | 0.807451  | 0.000085  | 0.007147  |
| N  | -2.067521 | -0.008819 | -0.006643 |
| C  | -3.241259 | -0.012464 | -0.012250 |

Frequencies

34.48  
53.09  
60.48  
67.89  
125.04  
937.31

938.60  
939.30  
993.02  
993.86  
2075.38  
2261.12  
2265.62  
2265.81  
2272.02

**vdW3: H<sub>3</sub>Si--HNC**

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 2.629271  | -0.307361 | 0.063597  |
| H  | 3.023853  | 1.025562  | 0.556565  |
| H  | 3.036648  | -1.385641 | 0.983791  |
| H  | 3.086943  | -0.549644 | -1.317467 |
| H  | -0.232844 | -0.323816 | 0.033468  |
| N  | -1.234361 | -0.330237 | 0.021798  |
| C  | -2.403810 | -0.333162 | 0.012848  |

**Frequencies**

71.94  
89.30  
95.40  
185.37  
192.36  
554.67  
560.89  
778.27  
949.96  
951.90  
2060.12  
2241.24  
2279.34  
2280.85  
3690.63

**vdW4: H<sub>3</sub>Si--HCN**

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 0.002379  | 0.008807  | -2.205397 |
| H  | -0.105881 | 1.418020  | -2.630405 |
| H  | 1.274948  | -0.599958 | -2.639218 |
| H  | -1.163095 | -0.786795 | -2.637753 |
| H  | 0.000071  | -0.003791 | 0.973943  |
| C  | -0.001061 | -0.005865 | 2.040596  |
| N  | -0.002188 | -0.008010 | 3.194890  |

**Frequencies**

50.09  
83.00  
88.35  
264.20

266.31  
776.72  
777.07  
786.43  
953.30  
954.20  
2123.46  
2237.28  
2274.60  
2275.69  
3417.51

TRANSITION STATES

**TS1: Reactants - SiH<sub>3</sub>CN+H**

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 0.001424  | 0.002548  | -0.002595 |
| H  | 1.479798  | 0.002376  | -0.000167 |
| H  | -0.544678 | 1.376261  | 0.000818  |
| H  | -0.543469 | -0.799465 | -1.118955 |
| H  | -0.440303 | -0.649813 | 1.261801  |
| C  | 0.765822  | 1.125996  | -2.206222 |
| N  | 1.111610  | 1.634264  | -3.202514 |

Frequencies

91.69 i  
84.88  
110.11  
125.42  
169.83  
819.18  
918.17  
920.25  
973.08  
974.41  
2115.83  
2166.81  
2234.35  
2242.36  
2242.73

**TS2: vdw2 - vdw3**

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 1.103588  | 0.003612  | 0.005183  |
| H  | 1.538677  | 1.327387  | 0.488278  |
| H  | 1.544853  | -1.071465 | 0.913234  |
| H  | 1.557811  | -0.240014 | -1.376634 |
| H  | -0.478576 | -0.002303 | -0.005499 |
| N  | -2.042065 | -0.006994 | -0.010514 |
| C  | -3.224288 | -0.010223 | -0.014048 |

Frequencies

1286.93 i

93.12  
97.73  
259.43  
259.59  
494.89  
896.10  
903.82  
903.85  
958.40  
958.46  
2035.51  
2255.87  
2278.81  
2278.87

**TS3: vdW1 - SiH<sub>3</sub>NC+H**

|    |           |           |           |
|----|-----------|-----------|-----------|
| Si | 0.027243  | 0.043509  | -0.119708 |
| H  | 1.497872  | -0.007416 | 0.020696  |
| H  | -0.657193 | 1.346136  | 0.020853  |
| H  | -0.657147 | -1.046052 | -0.847392 |
| H  | -0.297523 | -0.473760 | 1.305404  |
| N  | 0.469303  | 0.747550  | -2.059492 |
| C  | 0.715409  | 1.139358  | -3.139144 |

**Frequencies**

724.19 i  
179.20  
180.94  
336.66  
342.50  
641.94  
874.88  
875.07  
973.85  
974.61  
1759.77  
2045.35  
2211.71  
2234.88  
2235.98



**Table S4.** Optimized Cartesian coordinates (Å), and vibrational frequencies (cm<sup>-1</sup>) of reactants, products, intermediates, and transition states involved in the cyano radical (CN) plus methane (CH<sub>4</sub>) reaction.

REACTANTS

CH<sub>4</sub>

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.000013 | 0.000000  | 0.000013  |
| H | -0.000227 | -0.000001 | 1.086431  |
| H | 0.567349  | 0.852840  | -0.362039 |
| H | 0.455058  | -0.917677 | -0.362059 |
| H | -1.022166 | 0.064838  | -0.362349 |

Frequencies

1350.96  
 1352.09  
 1352.14  
 1575.44  
 1575.59  
 3052.21  
 3164.65  
 3164.71  
 3164.88

PRODUCTS

CH<sub>3</sub>

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 0.000000  | 0.000107  | -0.000000 |
| H | -0.000000 | -1.075715 | 0.000000  |
| H | -0.000000 | 0.537804  | 0.931787  |
| H | -0.000000 | 0.537804  | -0.931787 |

Frequencies

528.87  
 1428.45  
 1432.31  
 3139.51  
 3323.05  
 3323.34

CH<sub>3</sub>CN

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.036660 | 0.063433  | -0.025912 |
| H | -0.031572 | 0.054295  | 1.061359  |
| H | 0.990224  | 0.054446  | -0.383253 |
| H | -0.542134 | -0.830361 | -0.383524 |
| C | -0.723361 | 1.252913  | -0.511498 |
| N | -1.268700 | 2.197693  | -0.897167 |

Frequencies

373.16  
 375.26  
 928.66

1068.00  
1068.40  
1422.45  
1490.02  
1490.37  
2302.21  
3076.43  
3152.88  
3153.02

CH<sub>3</sub>NC

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.039698 | 0.068783  | -0.028105 |
| H | -0.037902 | 0.065597  | 1.058469  |
| H | 0.985335  | 0.065674  | -0.388595 |
| H | -0.549501 | -0.820477 | -0.388629 |
| N | -0.709237 | 1.228454  | -0.501475 |
| C | -1.261198 | 2.184388  | -0.891660 |

Frequencies

271.95  
273.24  
957.05  
1157.97  
1158.20  
1467.58  
1507.93  
1508.09  
2202.58  
3075.32  
3155.69  
3156.06

INTERMEDIATES

vdW5: H<sub>4</sub>C--CN

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.001579 | -0.000352 | -2.005488 |
| H | 0.458541  | 0.916561  | -1.646705 |
| H | 0.562615  | -0.857647 | -1.647852 |
| H | -1.025945 | -0.060661 | -1.647424 |
| H | -0.001528 | 0.000342  | -3.092407 |
| C | -0.002653 | -0.003390 | 1.240952  |
| N | 0.004378  | 0.004278  | 2.413740  |

Frequencies

61.79  
73.60  
74.25  
101.80  
102.70  
1346.04  
1353.61

1353.66  
1573.54  
1573.89  
2087.97  
3047.17  
3160.30  
3160.80  
3160.86

**vdW6: H<sub>3</sub>CH--NC**

|   |           |           |           |
|---|-----------|-----------|-----------|
| N | 0.097922  | -0.157731 | 1.562292  |
| C | -0.041146 | 0.097261  | 2.698852  |
| H | 0.041061  | -0.031521 | -1.158094 |
| C | 0.000155  | 0.052065  | -2.240401 |
| H | 0.244118  | 1.068891  | -2.536015 |
| H | 0.715404  | -0.634595 | -2.685014 |
| H | -1.000013 | -0.194402 | -2.586429 |

**Frequencies**

54.03  
84.07  
99.13  
102.73  
126.29  
1349.29  
1356.10  
1357.18  
1577.57  
1578.45  
2082.13  
3051.63  
3164.07  
3164.20  
3168.65

**vdW7: H<sub>3</sub>C--HNC**

|   |           |           |           |
|---|-----------|-----------|-----------|
| N | 0.029318  | -0.019581 | 0.902686  |
| C | 0.027700  | -0.034147 | 2.071876  |
| H | 0.023403  | -0.002110 | -0.101195 |
| C | -0.003574 | 0.059457  | -2.350680 |
| H | 0.264997  | 1.102444  | -2.371618 |
| H | 0.761160  | -0.690329 | -2.465235 |
| H | -1.041199 | -0.224914 | -2.403298 |

**Frequencies**

97.88  
109.52  
120.52  
223.90  
224.07

600.69  
600.91  
652.63  
1429.12  
1429.23  
2061.03  
3128.12  
3311.98  
3312.80  
3649.30

**vdW8: H<sub>3</sub>C--HCN**

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.001771 | -0.000052 | 1.273438  |
| N | -0.000395 | 0.000010  | 2.427845  |
| H | -0.002997 | -0.000094 | 0.204987  |
| C | 0.001305  | 0.000065  | -2.287472 |
| H | 1.077048  | 0.000058  | -2.332229 |
| H | -0.536407 | -0.931478 | -2.335587 |
| H | -0.536416 | 0.931607  | -2.335502 |

**Frequencies**

88.24  
96.57  
96.65  
207.31  
207.40  
598.75  
795.86  
795.86  
1428.16  
1428.26  
2123.16  
3133.45  
3314.87  
3315.08  
3392.50

**TRANSITION STATES**

**TS5: Reactants – vdW8**

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.000003 | 0.000006  | 0.846690  |
| N | 0.000021  | 0.000016  | 2.016479  |
| H | -0.000024 | -0.000026 | -1.060099 |
| C | -0.000003 | -0.000004 | -2.170342 |
| H | 1.032724  | 0.000003  | -2.504923 |
| H | -0.516357 | -0.894360 | -2.504969 |
| H | -0.516357 | 0.894365  | -2.504935 |

**Frequencies**

55.75 i  
92.63

93.04  
200.16  
201.26  
1308.22  
1320.96  
1321.46  
1522.03  
1524.03  
2127.72  
2647.31  
3088.13  
3187.77  
3188.10

**TS6: vdW6 – vdW7**

|   |           |           |           |
|---|-----------|-----------|-----------|
| N | 0.058324  | -0.076794 | 0.665553  |
| C | -0.017617 | 0.058761  | 1.837401  |
| H | 0.041312  | -0.035114 | -0.726756 |
| C | 0.000995  | 0.048631  | -1.947592 |
| H | 0.255529  | 1.080645  | -2.160301 |
| H | 0.739630  | -0.666610 | -2.291851 |
| H | -1.018567 | -0.213979 | -2.206084 |

Frequencies

1854.08 i  
40.30  
47.69  
413.32  
422.09  
593.75  
1205.22  
1208.27  
1247.42  
1450.69  
1454.21  
2051.25  
3083.09  
3218.43  
3219.86

**TS7: vdW5 - CH<sub>3</sub>CN+H**

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -0.001460 | -0.000514 | -1.416434 |
| H | 0.484275  | 0.967709  | -1.440794 |
| H | 0.594092  | -0.905306 | -1.441335 |
| H | -1.082809 | -0.063971 | -1.440768 |
| H | -0.001544 | 0.000049  | -2.759853 |
| C | -0.000583 | -0.000443 | 0.407283  |
| N | 0.001858  | 0.001664  | 1.570084  |

Frequencies

1282.86 i  
160.23  
160.28  
621.18  
621.80  
662.20  
1307.16  
1307.83  
1377.54  
1378.14  
1410.20  
2190.86  
3043.01  
3218.38  
3218.58

**TS8: Reactants - CH<sub>3</sub>NC+H**

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | 0.000783  | -0.001860 | -1.329106 |
| H | 0.865214  | 0.646387  | -1.382686 |
| H | 0.129991  | -1.074495 | -1.384182 |
| H | -0.992932 | 0.422628  | -1.381168 |
| H | -0.000867 | 0.000434  | -2.709842 |
| N | 0.002044  | -0.003268 | 0.438396  |
| C | -0.001239 | 0.003940  | 1.617729  |

**Frequencies**

1298.83 i  
102.85  
102.96  
546.82  
547.36  
670.32  
1263.54  
1263.84  
1367.91  
1388.12  
1389.01  
2080.40  
3067.94  
3238.22  
3238.54

## References

- (1) Walsh, R. Bond Dissociation Energy Values in Silicon-Containing Compounds and Some of Their Implications. *Acc. Chem. Res.* **1981**, *14*, 246-252.
- (2) Ruscic, B. Active Thermochemical Tables: Sequential Bond Dissociation Enthalpies of Methane, Ethane, and Methanol and the Related Thermochemistry. *J. Phys. Chem. A* **2015**, *119*, 7810-7837.
- (3) Costes, M.; Naulin, C.; Dorthe, G. The Dissociation Energy of the CN Radical Determined from the CN Internal Energy Release of the C + NO Yielding CN + O Reaction. *Astron. Astrophys.* **1990**, *232*, 270-276.
- (4) Huang, Y.; Barts, S. A.; Halpern, J. B. Heat of Formation of the Cyanogen Radical. *J. Phys. Chem.* **1992**, *96*, 425-428.