Supplementary Information

Gaseous Reaction Mechanism between Two H₂CN Radicals

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**Table 1:** Total (a.u.) and relative energies (kJ/mol) of the reactants and all isomers, products and transition states for CH$_2$N+CH$_2$N reaction at the B3LYP/6-31++G(d,p) and CCSD(T)/6-311++G(2df,p)//B3LYP/6-31++G(d,p)+ZPVE levels. The ZPVE energies are obtained from the B3LYP/6-31++G(d,p) calculations.

<table>
<thead>
<tr>
<th>species</th>
<th>B3LYP/6-31++G(d,p)</th>
<th>ZPVE</th>
<th>CCSD(T)/6-311++G(2df,p)</th>
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<tr>
<td>R:CH$_2$N+CH$_2$N</td>
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<td>0.050502(0.0)</td>
<td>-187.6284684(0.0)</td>
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<tr>
<td>L1</td>
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<td>-187.7162653(-202.0)</td>
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<tr>
<td>L2</td>
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<td>-187.6744563(-120.9)</td>
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<tr>
<td>L3</td>
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<td>L4</td>
<td>-187.9739072(26.8)</td>
<td>0.059989(25.1)</td>
<td>-187.6198636(22.6)</td>
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<tr>
<td>L5</td>
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<td>0.062544(31.8)</td>
<td>-187.7439339(-303.3)</td>
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<tr>
<td>L6</td>
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<td>-187.7011414(-190.8)</td>
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<tr>
<td>r1</td>
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<td>0.062907(32.6)</td>
<td>-187.7005261(-189.1)</td>
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<tr>
<td>r2</td>
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<td>0.061567(28.9)</td>
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<tr>
<td>r3</td>
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<td>r4</td>
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<td>r5</td>
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<td>-187.5682437(158.2)</td>
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<td>TSL1/L4</td>
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<td>TSr1/P1</td>
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<td>TSr2/L5</td>
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<td>TSr2/r7</td>
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<td>0.056973(17.2)</td>
<td>-187.5744697(141.8)</td>
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<td>0.056470(15.5)</td>
<td>-187.5885082(105.0)</td>
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<td>TSr4/L6</td>
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<td>0.060538(26.4)</td>
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<td>TSr4/r5</td>
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<td>-187.5735438(144.3)</td>
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<tr>
<td>TSr5/r6</td>
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<td>-187.5780705(132.2)</td>
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<tr>
<td>$^3$L1c</td>
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<td>$^3$L1t</td>
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<td>0.057223(17.6)</td>
<td>-187.6165961(31.0)</td>
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<table>
<thead>
<tr>
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<th>Energy</th>
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<td>3L2</td>
<td>-187.9741635(26.4)</td>
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<td>3L3</td>
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<tr>
<td>3L4</td>
<td>-187.9655223(49.0)</td>
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<td>3L5</td>
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<td>3r1</td>
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<td>-187.5991314(77.0)[102.5]</td>
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<td>3r2</td>
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<td>3TSR/L1</td>
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<td>-187.934743(129.7)</td>
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<td>3TSL1/L3</td>
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<tr>
<td>3TSL1/L4</td>
<td>-187.8798049(274.1)</td>
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<tr>
<td>3TSL1/r1</td>
<td>-187.9113965(190.8)</td>
<td>0.057080(17.2)</td>
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<tr>
<td>3TSL1/r2</td>
<td>-187.9404068(114.6)</td>
<td>0.056045(14.6)</td>
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<td>3TSL5/P3</td>
<td>-187.9461129(100.0)</td>
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<tr>
<td>P1: C2H4 + N2</td>
<td>-188.129485(-381.6)</td>
<td>0.05658(15.9)</td>
<td>-187.7935157(-433.5)[-417.6]</td>
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<tr>
<td>P2: 2HCN H2</td>
<td>-188.040221(-147.3)</td>
<td>0.042782(-20.1)</td>
<td>-187.7070036(-206.3)[-226.4]</td>
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<tr>
<td>P3: CH2NH + HCN</td>
<td>-188.0713648(-228.9)</td>
<td>0.056263(15.1)</td>
<td>-187.7301958(-266.9)[-251.9]</td>
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<tr>
<td>P3*: CH2NH + HCN</td>
<td>-187.9402274(115.5)</td>
<td>0.049461(-2.9)</td>
<td>-187.5881553(105.9)[102.9]</td>
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<tr>
<td>P4: CH2NNCH + H</td>
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<tr>
<td>P5: H + r-CH2NNCH</td>
<td>-187.8952447(233.5)</td>
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**SITable 2:** Vibrational frequencies and moments of inertia for reactants, intermediates, and transition states predicted at the B3LYP/6-311++G(d,p) level of theory.

<table>
<thead>
<tr>
<th>Species</th>
<th>Moments of inertia (a.u.)</th>
<th>Frequencies (cm(^{-1}))</th>
</tr>
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<tr>
<td>H(_2)CN</td>
<td>6.3, 46.4, 52.7</td>
<td>939, 994, 1387, 1727, 2988, 3048</td>
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<tr>
<td>L(_1)</td>
<td>35.2, 337.2, 372.4</td>
<td>82, 376, 619, 668, 867, 877, 1053, 1054, 1183, 1238, 1444, 1456, 1680, 1710, 3089, 3093, 3219, 3219</td>
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<tr>
<td>r(_1)</td>
<td>126.2, 131.6, 234.9</td>
<td>312, 753, 847, 917, 1001, 1022, 1060, 1085, 1151, 1274, 1285, 1460, 1473, 1576, 3068, 3073, 3122, 3136</td>
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<tr>
<td>TSL(_1)/r(_1)</td>
<td>107.4, 170.9, 252.6</td>
<td>i801, 552, 683, 738, 854, 982, 991, 1090, 1136, 1213, 1253, 1386, 1515, 1531, 3109, 3110, 32145, 3217</td>
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<tr>
<td>TS(_1)/P(_1)</td>
<td>102.2, 217.2, 296.2</td>
<td>i498, 386, 529, 628, 736, 835, 952, 992, 1100, 1195, 1288, 1501, 1514, 1869, 2953, 3118, 3131, 3282</td>
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</tbody>
</table>
SITable 3a: Rate constants (k×10^{12} in cm^3 molecule^{-1} s^{-1}) with relative transition state TSL1/r1 shifted by +/-2 and +/-5 kJ/mol at 298 K and 600 K in various pressures (P in mbar) from the master equation rate constant calculations at the G3B3//B3LYP/6-31++G(d,p) level.

<table>
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<td>G3B3 +2</td>
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<td>+5</td>
<td>-5</td>
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<tr>
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SITable 3b: Rate constants (k×10^{12} in cm^3 molecule^{-1} s^{-1}) with relative transition state TSL1/r1 shifted by +/-2 and +/-5 kJ/mol at 45 K in low pressures (P in mbar) from the master equation rate constant calculations at the G3B3//B3LYP/6-31++G(d,p) level.

<p>| | | | | |</p>
<table>
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<td>G3B3 +2</td>
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<td>+5</td>
<td>-5</td>
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<tr>
<td>0.001mbar</td>
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</table>
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3TSL/r2 (C1)  \[ N_4C_3N_2C_1 = -105.84 \]
\[ H_4C_3N_1H_2 = -177.73 \]
\[ H_5C_3N_1H_2 = -3.30 \]
\[ H_7C_3N_2C_1 = 3.26 \]
\[ H_8C_3N_2C_1 = 146.00 \]

3TSL/P3 (C2)
\[ H_4C_3N_1H_2 = -171.32 \]
\[ H_5C_3N_1H_2 = 1.447 \]
\[ H_6C_3N_1H_2 = 1.195 \]

\[ 1.088 \]
\[ 1.083 \]
\[ 3TSL1/r2(C1) \]
\[ N_4C_3N_2C_1 = -105.84 \]
\[ H_4C_3N_1H_2 = -177.73 \]
\[ H_5C_3N_1H_2 = -3.30 \]
\[ H_7C_3N_2C_1 = 3.26 \]
\[ H_8C_3N_2C_1 = 146.00 \]
Master equation rate constant calculation

For a bimolecular reaction system with $M$ wells (intermediates) involved, the master equation can be written in the form of a set of coupled integral-differential equations:

$$\frac{d n_i(E)}{dt} = Z \frac{E}{E_0} P_i(E, E') n_i(E) dE - Z n_i(E) - \sum_{j \neq i}^M k_{j,i}(E) n_j(E) + \sum_{j \neq i}^M k_{i,j}(E) n_j(E) - k_{di}(E) n_i(E) + K_{Ri} k_{di}(E) f_i(E) n_{R1} n_{R2} - k_{pi}(E) n_i(E) \quad (i = 1, ..., M)$$

(1)

where $t$ is the time, $Z$ is the collision number per unit time, $n_i(E)$ is the number density of molecule in well $i$ at energy $E$, $E_0$ is the ground-state energy for well $i$, $M$ is the number of wells in the reaction system, $P_i(E, E')$ is the collision transfer probability that a molecule in well $i$ with energy $E$, will be transferred to a state with energy $E'$, $k_{j,i}(E)$ is the microcanonical rate constant for isomerization from well $j$ to well $i$ at energy $E$, $k_{di}(E)$ and $k_{pi}(E)$ are the microcanonical rate constants for dissociation from well $i$ to the bimolecular “reactants” and products, respectively; $n_{R1}$ and $n_{R2}$ are the number densities of reactants, and $K_{Ri}$ is the equilibrium constant for the reaction from reactants to the molecules in well $i$. The function $f_i(E)$ is the equilibrium energy distribution in well $i$ at temperature $T$:

$$f_i(E) = \rho_i(E) e^{-\beta E} / Q_i(T)$$

(2)

where $\rho_i(E)$ is the vibrational-rotational density of states of a molecule in well $i$ at energy $E$, $\beta = 1/k_B T$ with $k_B$ being the Boltzmann constant, $Q_i(T)$ is the vibrational-rotational partition function for the $i$th well. We generally assume that the number density of one reactant is much smaller than the number density of the other reactant, and both of them are much smaller than the number density of the bath gas, $n_B$, i.e. $n_B >> n_{R2} >> n_{R1}$. Thus, the reaction from reactants to the wells is a quasi first order reaction with respect to $n_{R1}$. An additional equation for $n_{R1}$ makes
By solving the differential equation set of (1) and (3), one can obtain the time-dependent, temperature-dependent and pressure-dependent kinetics of the reaction system. The solution of the master equation is somewhat tricky due to the numerical round off errors. We chose the method of directly solving the ordinary differential equations of (1) and (3) to calculate the evolution of number densities with time of reactant $n_{R1}$ and molecules in each well. The final overall rate constant is determined at the half consumption of $n_{R1}$. The microcanonical rate constant $k(E)$ was calculated by using the RRKM (Rice, Ramsperger, Kassel, Marcus) method. The collision transfer probability $P(E,E')$ was calculated from the exponential down model with average transfer energy $\Delta E_d=100\text{cm}^{-1}$ and Ar was employed as buffer gases as in the Nizamov et al.’s experiment. The Lennard-Jones parameters for intermediates are calculated from the empirical method.