Supplementary Material (ESI) for *PCCP*

Supplementary Information

Gaseous Reaction Mechanism between Two H_2CN Radicals

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SITable 1: Total (a.u.) and relative energies (kJ/mol) of the reactants and all isomers, products and transition states for CH_2N+CH_2N 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.

species	B3LYP/6-31++G(d,p)	ZPVE	CCSD(T)/6-311++G(2df,p) //B3LYP/6-31++G(d,p)[+ZPVE]
R:CH_2N+CH_2N	**-187.9841318(0.0)**	**0.050502(0.0)**	**-187.6284684(0.0)**
L1	-188.0651894(-213.0)	0.061341(28.5)	-187.7162665(-230.5)[-202.0]
L2	-188.0257352(-109.2)	0.060072(25.1)	-187.6744563(-120.9)[-95.8]
L3	-188.0028401(-48.9)	0.061086(27.6)	-187.6530118(-64.4)[-36.8]
L4	-187.9739072(26.8)	0.059989(25.1)	-187.6198636(22.6)[47.7]
L5	-188.091735(--282.4)	0.062544(31.8)	-187.7439339(-303.3)[-271.5]
L6	-188.0478088(-167.4)	0.061496(28.9)	-187.7011414(-190.8)[-161.9]
r1	-188.0455836(-161.5)	0.062907(32.6)	-187.7005261(-189.1)[-156.5]
r2	-188.0063662(-58.6)	0.061567(28.9)	-187.6550615(-69.9)[-41.0]
r3	-188.0041246(-52.3)	0.061994(30.1)	-187.6558703(-72.0)[-41.9]
r4	-188.0431003(-154.8)	0.063442(33.9)	-187.6964698(-178.7)[-144.8]
r5	-187.9858485(-4.6)	0.063316(33.5)	-187.6370746(-22.6)[10.9]
r6	-188.021885(-99.2)	0.063345(33.9)	-187.6740769(-119.7)[-85.8]
r7	-187.9887224(-12.6)	0.060785(27.2)	-187.6361967(-20.1)[7.1]
r8	-187.9466634(98.3)	0.056885(16.7)	-187.6081378(53.6)[70.3]
TSL1/L2	-187.9656648(48.5)	0.056432(15.5)	-187.6154833(33.9)[49.4]
TSL1/L3	-187.9178852(174.1)	0.055368(13.0)	-187.5682437(158.2)[171.1]
TSL1/L4	-187.9672659(44.4)	0.056028(14.6)	-187.6156187(33.9)[48.5]
TSL1/r1	-187.9922468(-21.3)	0.060540(26.4)	-187.6450548(-43.5)[-17.2]
TSL1/r2	-187.9757382(22.2)	0.059425(23.4)	-187.6225257(15.5)[38.9]
TSL1/P2	-187.9611124(60.2)	0.048629(-5.0)	-187.6137232(38.9)[33.9]
TSL1/P3	-187.9574079(70.3)	0.052365(5.0)	-187.6138442(38.5)[43.5]
TSL2/L4	-187.903515(211.7)	0.054394(10.0)	-187.550018(205.9)[215.9]
TSr1/r3	-187.9322084(136.4)	0.056353(15.5)	-187.5844229(115.5)[131.0]
TSr1/r4	-187.8691104(302.1)	0.054815(11.3)	-187.5239576(274.5)[285.8]
TSr1/P1	-187.9746071(25.1)	0.059255(23.0)	-187.6411186(-33.0)[-10.0]
TSr2/L5	-187.9253686(154.4)	0.057453(18.4)	-187.5750217(140.2)[158.6]
TSr2/r7	-187.9151901(181.2)	0.056973(17.2)	-187.5744697(141.8)[159.0]
TSr3/r4	-187.9349283(129.3)	0.056470(15.5)	-187.5885082(105.0)[120.5]
TSr4/L6	-187.9800099(10.9)	0.060538(26.4)	-187.6355505(-18.4)[7.9]
TSr4/r5	-187.9229598(160.7)	0.057386(18.0)	-187.5735438(144.3)[162.3]
TSr5/r6	-187.9287746(145.2)	0.058142(20.1)	-187.5780705(132.2)[152.3]
^{3}L1c	-187.9747766(24.7)	0.057373(18.0)	-187.6092175(50.6)[68.6]
^{3}L1t	-187.9834444(1.7)	0.057223(17.6)	-187.6165961(31.0)[48.5]

^{3}L2	-187.9741635(26.4)	0.057805(19.2)	-187.6139609(38.1)[57.3]
^{3}L3	-187.9515959(85.4)	0.058762(21.8)	-187.5946732(88.7)[110.5]
^{3}L4	-187.9655223(49.0)	0.058170(20.1)	-187.6050587(61.5)[81.6]
^{3}L5	-187.987259(-8.4)	0.051459(2.5)	-187.6323372(-10.0)[-7.5]
^{3}r1	-187.9541483(78.7)	0.060240(25.5)	-187.5991314(77.0)[102.5]
^{3}r2	-187.9538255(79.5)	0.057736(-18.8)	-187.5978995(80.3)[61.5]
^{3}TSR/L1	-187.9529365(82.0)	0.054589(10.9)	-187.5924232(94.6)[105.4]
^{3}TSL1/L1c	-187.9705686(35.6)	0.056846(16.7)	-187.6078876(54.0)[70.7]
^{3}TSL1/L2	-187.934743(129.7)	0.053115(6.7)	-187.5751821(139.7)[146.4]
^{3}TSL1/L3	-187.8858873(257.7)	0.052634(5.4)	-187.526285(268.2)[273.6]
^{3}TSL1/L4	-187.8798049(274.1)	0.052001(3.8)	-187.5174396(291.6)[295.4]
^{3}TSL1/r1	-187.9113965(190.8)	0.057080(17.2)	-187.5530123(197.9)[215.1]
^{3}TSL1/r2	-187.9404068(114.6)	0.056045(14.6)	-187.5804363(125.9)[140.6]
^{3}TSL5/P3	-187.9461129(100.0)	0.048077(-6.3)	-187.5812582(123.8)[117.6]
P1: $C_2H_4+N_2$	-188.129485(-381.6)	0.05658(15.9)	-187.7935157(-433.5)[-417.6]
P2:2HCN H_2	-188.040221(-147.3)	0.042782(-20.1)	-187.7070036(-206.3)[-226.4]
P3:CH_2NH+HCN	-188.0713648(-228.9)	0.056263(15.1)	-187.7301958(-266.9)[-251.9]
P3':$^3CH_2NH$+HCN	-187.9402274(115.5)	0.049461(-2.9)	-187.5881553(105.9)[102.9]
P4:CH_2NNCH+H	-187.8883214(251.5)	0.047065(-9.2)	-187.5378358(238.1)[228.9]
P5:H+r-CH_2NNCH	-187.8952447(233.5)	0.048965(-4.2)	-187.5473456(213.0)[208.8]

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.

Species	Moments of inertia (a.u.)	Frequencies (cm^{-1})
H_2CN	6.3, 46.4, 52.7	939, 994, 1387, 1727, 2988, 3048
L1	35.2, 337.2, 372.4	82, 376, 619, 668, 867, 877, 1053, 1054, 1183, 1238, 1444, 1456, 1680, 1710, 3089, 3093, 3219, 3219
r1	126.2, 131.6, 234.9	312, 753, 847, 917, 1001, 1022, 1060, 1085, 1151, 1274, 1285, 1460, 1473, 1576, 3068, 3073, 3122, 3136
TSL1/r1	107.4, 170.9, 252.6	i801, 552, 683, 738, 854, 982, 991, 1090, 1136, 1213, 1253, 1386, 1515, 1531, 3109, 3110, 32145, 3217
TSr1/P1	102.2, 217.2, 296.2	i498, 386, 529, 628, 736, 835, 952, 992, 1100, 1195, 1288, 1501, 1514, 1869, 2953, 3118, 3131, 3282

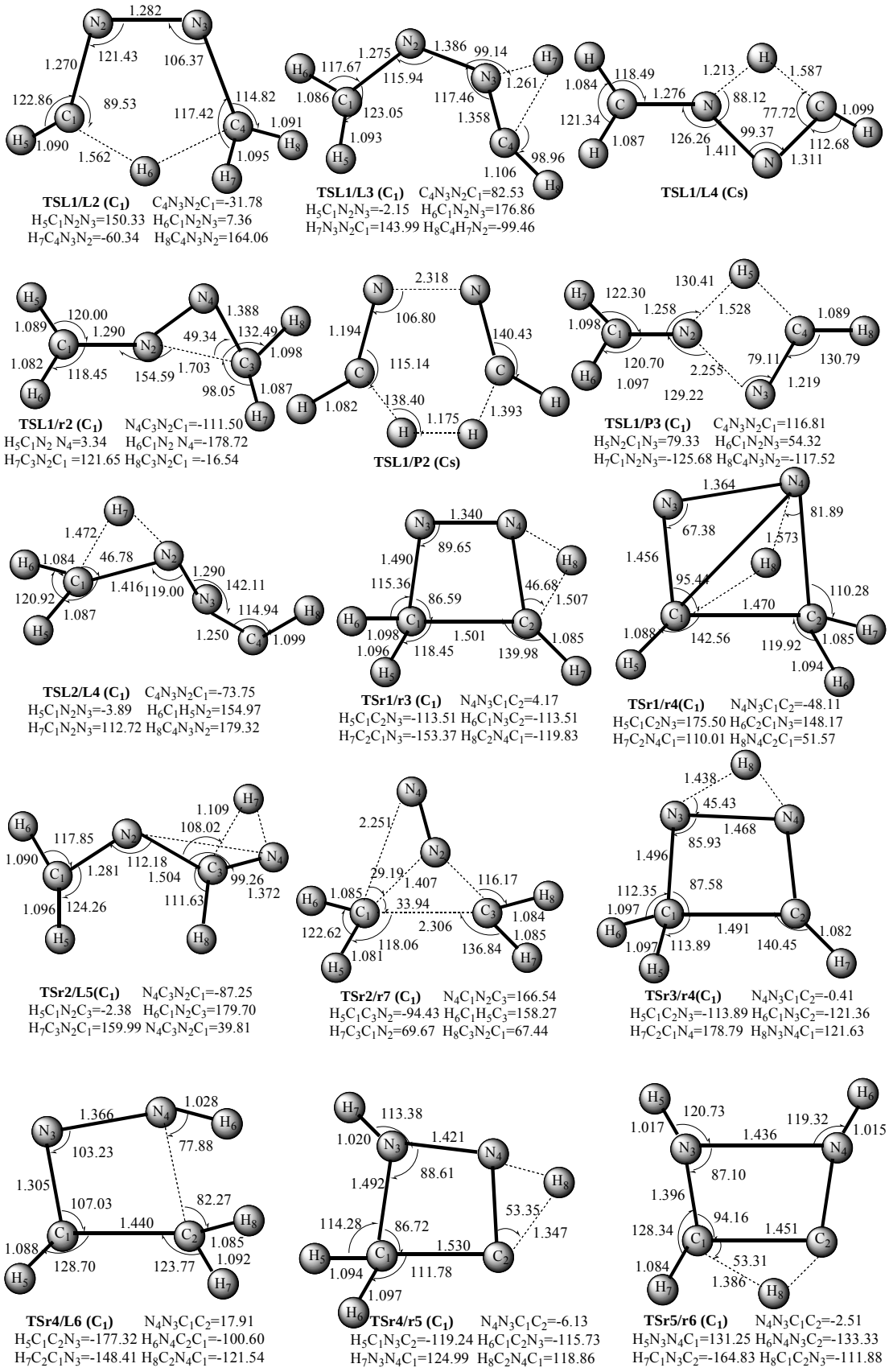
SITable 3a: Rate constants ($k\times10^{12}$ in $cm^3molecule^{-1}s^{-1}$) with relative transition state **TSL1/r1** shifted by +/-2 and +/-5 kJ/mol at 298 K and 600 K in various pressures (P in mbar) from the master equation rate constant calculations at the G3B3//B3LYP/6-31++G(d,p) level.

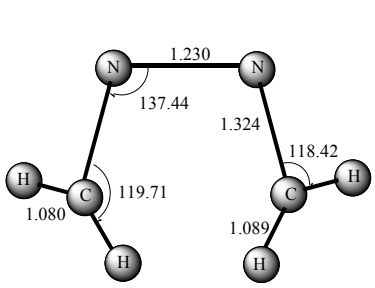
	298K					600K				
	G3B3	+2	-2	+5	-5	G3B3	+2	-2	+5	-5
0.67mbar	0.8856	0.8609	0.9092	0.8248	0.9306	0.0784	0.0677	0.0885	0.0510	0.0977
6.67	2.8107	2.7989	2.8223	2.7820	2.8330	0.0926	0.0786	0.1053	0.0565	0.1165
13.33	3.8885	3.8795	3.8973	3.8668	3.9056	0.0953	0.0805	0.1087	0.0574	0.1205
66.66	7.4383	7.4340	7.4427	7.4281	7.4470	0.0993	0.0831	0.1140	0.0584	0.1266
133.32	9.3336	9.3306	9.3368	9.3266	9.3399	0.1005	0.0838	0.1155	0.0586	0.1285
266.64	11.3297	11.3276	11.3319	11.3250	11.3342	0.1014	0.0843	0.1169	0.0588	0.1301
666.61	13.9205	13.9194	13.9218	13.9180	13.9232	0.1024	0.0849	0.1184	0.0590	0.1322
1013.25	15.0192	15.0184	15.0201	15.0174	15.0212	0.1028	0.0851	0.1191	0.0591	0.1330
1199.90	15.4396	15.4389	15.4405	15.4380	15.4414	0.1030	0.0852	0.1193	0.0590	0.1334
1467.00	15.9190	15.9184	15.9197	15.9177	15.9205	0.1031	0.0852	0.1196	0.0590	0.1338

SITable 3b: Rate constants ($k\times10^{12}$ in $cm^3molecule^{-1}s^{-1}$) 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.

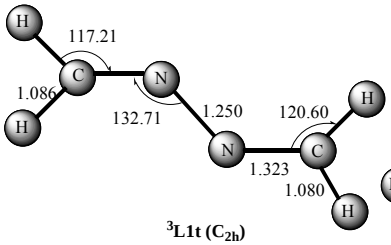
	G3B3	+2	-2	+5	-5
0.001mbar	57.6726	57.1138	58.1035	56.0029	58.4284
0.01	59.9527	59.7814	60.0978	59.4883	60.2155
0.07	62.5706	62.5640	62.5768	62.5540	62.5821
0.13	62.8757	62.8737	62.8776	62.8707	62.8793
0.40	63.1079	63.1076	63.1081	63.1071	63.1084
0.67	63.1580	63.1578	63.1581	63.1577	63.1582

SIFigure 1:

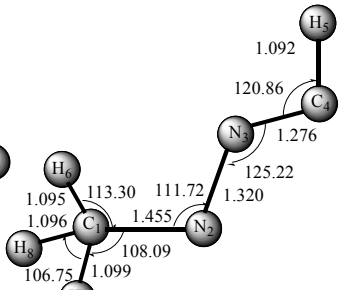

TSL1/L2 (C1) C4N3N2C1=-31.78
H5C1N2N3=150.33 H6C1N2N3=7.36
H7C4N3N2=-60.34 H8C4N3N2=164.06
TSL1/L3 (C1) C4N3N2C1=82.53
H5C1N2N3=-2.15 H6C1N2N3=176.86
H7N3N2C1=143.99 H8C4H7N2=-99.46
TSL1/L4 (Cs)
TSL1/r2 (C1) N4C3N2C1=-111.50
H5C1N2 N4=3.34 H6C1N2 N4=-178.72
H7C3N2C1 =121.65 H8C3N2C1 =-16.54
TSL1/P2 (Cs)
TSL1/P3 (C1) C4N3N2C1=116.81
H5N2C1N3=79.33 H6C1N2N3=54.32
H7C1N2N3=-125.68 H8C4N3N2=-117.52
TSL2/L4 (C1) C4N3N2C1=-73.75
H5C1N2N3=-3.89 H6C1H5N2=154.97
H7C1N2N3=112.72 H8C4N3N2=179.32
TSr1/r3 (C1) N4N3C1C2=4.17
H5C1C2N3=-113.51 H6C1N3C2=-113.51
H7C2C1N3=-153.37 H8C2N4C1=-119.83
TSr1/r4(C1) N4N3C1C2=-48.11
H5C1C2N3=175.50 H6C2C1N3=148.17
H7C2N4C1=110.01 H8N4C2C1=51.57
TSr2/L5(C1) N4C3N2C1=-87.25
H5C1N2C3=-2.38 H6C1N2C3=179.70
H7C3N2C1=159.99 N4C3N2C1=39.81
TSr2/r7 (C1) N4C1N2C3=166.54
H5C1C3N2=-94.43 H6C1H5C3=158.27
H7C3C1N2=69.67 H8C3N2C1=67.44
TSr3/r4(C1) N4N3C1C2=-0.41
H5C1C2N3=-113.89 H6C1N3C2=-121.36
H7C2C1N4=178.79 H8N3N4C1=121.63
TSr4/L6 (C1) N4N3C1C2=17.91
H5C1C2N3=-177.32 H6N4C2C1=-100.60
H7C2C1N3=-148.41 H8C2N4C1=-121.54
TSr4/r5 (C1) N4N3C1C2=-6.13
H5C1N3C2=-119.24 H6C1C2N3=-115.73
H7N3N4C1=124.99 H8C2N4C1=118.86
TSr5/r6 (C1) N4N3C1C2=-2.51
H5N3N4C1=131.25 H6N4N3C2=-133.33
H7C1N3C2=-164.83 H8C1C2N3=-111.88



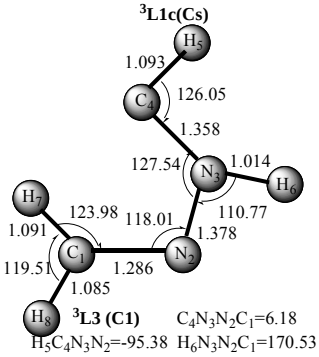
^{3}L1c(Cs)



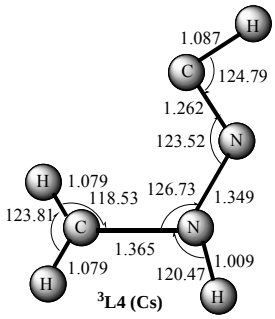
^{3}L1t (C_{2h})



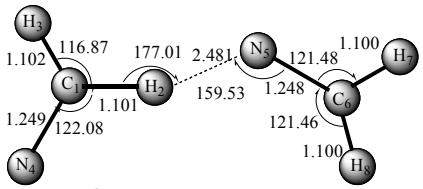
^{3}L2 (C1) $C_4N_3N_2C_1$=178.70
$H_5C_4N_3N_2$=179.88 $H_6C_1N_2N_3$=10.52
$H_7C_1N_2N_3$=-111.15 $H_8C_1H_7N_2$=116.09



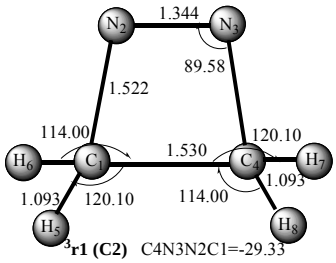
^{3}L3 (C1) $C_4N_3N_2C_1$=6.18
$H_5C_4N_3N_2$=-95.38 $H_6N_3N_2C_1$=170.53
$H_7C_1N_2N_3$=-2.50 $H_8C_1H_7N_2$=179.11



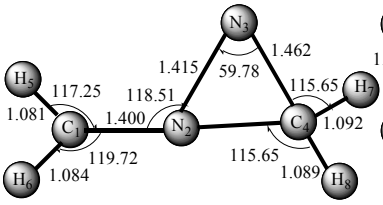
^{3}L4 (Cs)



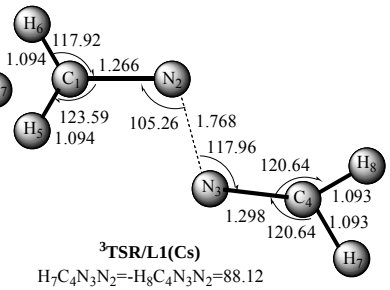
^{3}L5(C1) $N_4C_1H_2H_3$=-179.98
$N_5H_2C_1H_3$=3.14 $C_6N_5H_2C_1$=179.11
$H_7C_6N_5H_2$=97.87 $H_8C_6N_5H_7$=-179.98



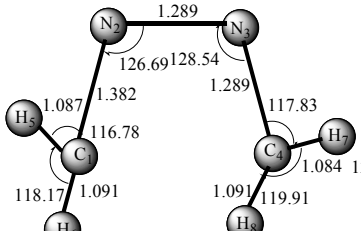
^{3}r1 (C2) C4N3N2C1=-29.33
$H_5C_1C_4N_3$=$H_7C_4C_1N_2$=-135.71
$H_6C_1C_4N_3$=$H_8C_4C_1N_2$=87.22



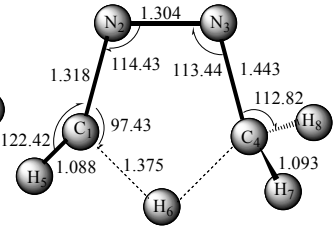
^{3}r2 (C1) $C_4N_3N_2C_1$=-116.26
$H_5C_1N_2N_3$=-150.22 $H_6C_1N_2C_4$=26.43
$H_7C_4N_3N_2$=110.80 $H_8C_4N_2C_1$=-144.04



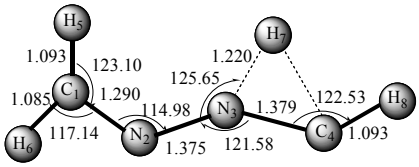
^{3}TSR/L1(Cs)
$H_7C_4N_3N_2$=-$H_8C_4N_3N_2$=88.12



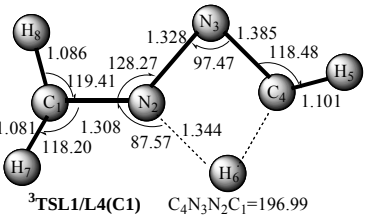
^{3}TSL1c/L1t(C1) $C_4N_3N_2C_1$=-51.32
$H_5C_1N_2N_3$=-120.76 $H_6C_1H_5N_2$=147.77
$H_7C_4N_3N_2$=178.23 $H_8C_4H_7N_3$=-117.41



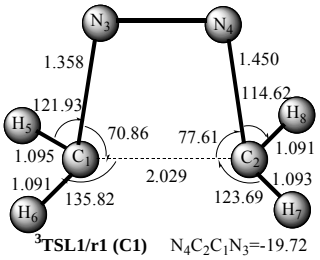
^{3}TSL1/L2(Cs)
$H_7C_4N_3N_2$=-$H_8N_4C_3C_2$=-115.81



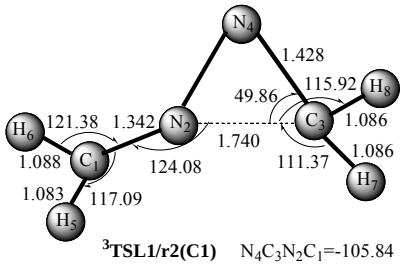
^{3}TSL1/L3 (C1) $C_4N_3N_2C_1$=-153.07
$H_5C_1N_2N_3$=2.45 $H_6C_1N_2N_3$=182.80
$H_7N_3N_2C_1$=-76.44 $H_8C_4N_3N_2$=-135.75



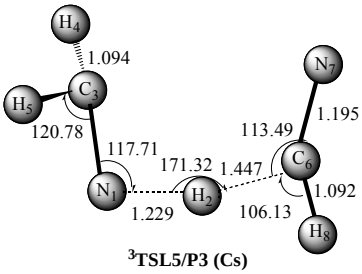
^{3}TSL1/L4(C1) $C_4N_3N_2C_1$=196.99
$H_5C_4N_3N_2$=-111.66 $H_6N_2C_4N_3$=-2.63
$H_7C_1N_2N_3$=-176.25 $H_8C_1N_2N_3$=5.47



^{3}TSL1/r1 (C1) $N_4C_2C_1N_3$=-19.72
$H_5C_1N_3C_2$=-78.48 $H_6C_1C_2N_3$=-108.77
$H_7C_2C_1N_4$=115.46 $H_8C_2N_4C_1$=94.86



^{3}TSL1/r2(C1) $N_4C_3N_2C_1$=-105.84
$H_5C_1N_2N_4$=-177.73 $H_6C_1N_2N_4$=-3.30
$H_7C_3N_2C_1$=3.26 $H_8C_3N_2C_1$=146.00



^{3}TSL5/P3 (Cs)
$H_4C_3N_1H_2$=-$H_5C_3N_1H_2$=89.58

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:

$$\frac{\mathrm{d}n_i(E)}{\mathrm{d}t} = Z\int_{E_{0i}}^{\infty} P_i(E,E')n_i(E')\mathrm{d}E' - Zn_i(E) - \sum_{j\neq i}^{M} k_{ji}(E)n_i(E) + \sum_{j\neq i}^{M} k_{ij}(E)n_j(E) - k_{di}(E)n_i(E) + K_{Ri}k_{di}(E)\,f_i(E)n_{R1}n_{R2} - k_{pi}(E)n_i(E) \qquad (i = I,...,M) \tag{1}$$

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_{0i} 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, $k_{ij}(E)$ 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:

$$f_i(E) = \rho_i(E)\mathrm{e}^{-\beta E} / Q_i(T) \tag{2}$$

where $\rho_i(E)$ is the vibrational-rotational density of states of a molecule in well i at energy E, $\beta = 1/k_BT$ with k_B being the Boltzmann constant, $Q_i(T)$ is the vibrational-rotational partition function for the ith 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

the problem completed:

$$\frac{dn_{R1}}{dt} = \sum_{i=I}^{M} \int_{E_{0i}}^{\infty} k_{di}(E) n_i(E) dE - n_{R1} n_{R2} \sum_{i=I}^{M} K_{Ri} \int_{E_{0i}}^{\infty} k_{di}(E) f_i(E) dE \qquad (3)$$

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 rand 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 ΔE_d=100cm^{-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.