

Supporting Information

Kinetics and Branching for the Reactions of N_2^+ with C_3H_4 Isomers at Low Temperatures and Implications for Titan's Atmosphere

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CONTENT:

The tables and text below correspond to supplementary material for the manuscript “Kinetics and Branching for the Reactions of N_2^+ with C_3H_4 Isomers at Low Temperatures and Implications for Titan's Atmosphere”. Please refer to manuscript for discussion of the results and significance of the material below.

TABLE S1: The possible reaction channels along with the calculated relative enthalpies for the N_2^+ + CH_3CCH reaction at 0 K. The enthalpy of formation of all species is calculated in the spin unrestricted CCSD/aug-cc-pVDZ framework including ZPVE corrections. All energies are relative to separated N_2^+ + CH_3CCH input channel. A comparison is presented with the CCSD(T)/CBS//B3LYP/ 6-311G** results of Mebel and Brandauk (2008) [1] with respect to the $CH_2CCH_2^+$ + N_2 channel.

No. of reaction	Reaction products	Relative enthalpy (eV)	Relative enthalpy (kJ/mol)	Relative enthalpy with respect to $CH_2CCH_2^+$ + N_2 (kJ/mol)	Relative enthalpy with respect to $CH_2CCH_2^+$ + N_2 as in [1] (kJ/mol)
1	N_2^+ + CH_3CCH (propyne input channel)	0.0	0.0	535.6	
2	N_2^+ + CH_2CCH_2 (allene input channel)	+0.014	+1.4	536.8	
3	$CH_2CCH_2^+$ + N_2	-5.551	-535.6	0.0	0.0
4	CH_3CCH^+ + N_2	-5.402	-521.3	14.2	58.2
5	c- $C_3H_4^+$ + N_2	-5.017	-484.1	51.5	90.4
7	c- $C_3H_3^+$ + H + N_2	-4.275	-412.5	123.0	158.6
8	l- $C_3H_3^+$ (CH_2CCH^+) + H + N_2	-3.087	-297.9	237.7	274.1
9	c- $C_3H_2^+$ + H ₂ + N_2	-3.390	-327.2	208.4	243.9
10	HCCCH ⁺ + H ₂ + N_2	-3.029	-292.0	243.5	270.7
11	CH_2CC^+ + H ₂ + N_2	-1.539	-148.5	387.0	
12	HCCC ⁺ + H ₂ + H + N_2	+1.012	+97.5	633.0	675.7
13	c- C_3H^+ + H ₂ + H + N_2	+1.866	+179.9	715.5	

[1] A. M. Mebel and A. D. Brandauk, Theoretical Study of Unimolecular Decomposition of Allene Cations. *J. Chem. Phys.* **2008**, *129*, 224311.

TABLE S2: The geometries, total electronic and zero-point vibrational energies along with the harmonic vibrational frequencies of the molecular species which are employed in Figure 2 of the main manuscript and in Table S1 of this supplement.

I. C₃H₄ (propyne, CH₃CCCH)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	-1.2580368969	-0.0000212697	0.0000000013
C	0.2218549965	-0.0000105470	-0.0000000144
C	1.4464316730	-0.0000018933	0.0000000053
H	2.5217469621	0.0000056756	0.0000000125
H	-1.6428729611	1.0130160884	-0.2015893423
H	-1.6428631366	-0.3319625429	0.9781131320
H	-1.6428606370	-0.6811255110	-0.7765237945
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -116.316555200972</i>			
<i>Zero point energy [Hartree]: 0.05485687</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
277.85; 277.99; 577.10; 577.10; 938.59; 1049.53; 1049.63; 1406.21; 1473.09; 1473.44; 2193.21; 3052.84; 3132.27; 3132.34; 3468.19			
II. C₃H₄⁺ (propyne cation, CH₃CCCH cation)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	-1.2685338713	-0.0400559984	0.0077669538
C	0.1777534602	-0.0334319535	0.0064100437
C	1.4455308294	0.0071500065	-0.0013056033
H	2.5328605313	0.0357341847	-0.0069555083
H	-1.5661739239	1.0158691322	-0.2019538113
H	-1.6587955007	-0.3126547028	1.0023274060
H	-1.6592415251	-0.6727106685	-0.8062894805
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -115.945092467496</i>			
<i>Zero point energy [Hartree]: 0.05185385</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
248.24; 316.37; 521.74; 622.56; 642.79; 867.71; 959.59; 1274.56; 1319.66; 1431.98; 2046.51; 2953.46; 3088.86; 3118.69; 3348.47			
III. C₃H₄ (allene, CH₂CCH₂)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	0.0000000000	0.0000000000	-0.0000000001
C	0.0000000000	0.0000000000	1.3267049256
C	0.0000000000	0.0000000000	-1.3267049259
H	0.0000000000	0.9389173481	1.8888122706
H	0.0000000000	-0.9389173481	1.8888122706
H	0.9389173482	0.0000000000	-1.8888122705
H	-0.9389173482	0.0000000000	-1.8888122705
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -116.316099174145</i>			
<i>Zero point energy [Hartree]: 0.05492045</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
323.32; 323.32; 862.61; 870.02; 870.03; 1008.52; 1008.52; 1088.97; 1431.73; 1484.71; 2026.41; 3156.22; 3156.75; 3248.08; 3248.08			
IV. C₃H₄⁺ (allene cation, CH₂CCH₂ cation)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	0.0000000000	0.0000000000	-0.0000000001
C	0.0000000000	0.0000000000	1.3491824565
C	0.0000000000	0.0000000000	-1.3491824568
H	0.0000000000	0.9496707295	1.9039968480
H	0.0000000000	-0.9496707295	1.9039968480
H	0.9496707295	0.0000000000	-1.9039968479
H	-0.9496707295	0.0000000000	-1.9039968479
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -115.950431929998</i>			
<i>Zero point energy [Hartree]: 0.05172587</i>			

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:
277.8; 278.18; 817.67; 852.47; 1010.49; 1022.86; 1047.19; 1321.96; 1480.34; 1931.75; 3104.49; 3116.33; 3213.66; 3229.82

V. c-C₃H₄⁺ (cyclopropene cation)

Geometry [xyz format, Angstroms]:

C	0.000000000	0.000000000	0.8238344376
C	0.000000000	0.6913870570	-0.4790995297
C	0.000000000	-0.6913870570	-0.4790995297
H	0.000000000	1.6237293160	-1.0504606701
H	0.000000000	-1.6237293160	-1.0504606701
H	0.9147641831	0.0000000000	1.4612429809
H	-0.9147641831	0.0000000000	1.4612429809

UCCSD/aug-cc-pVDZ energy [Hartree]: -115.930300665525

Zero point energy [Hartree]: 0.05122007

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:
586.37; 658.20; 839.75; 910.55; 985.67; 1024.25; 1090.84; 1227.54; 1259.95; 1480.07; 2925.39; 2957.76; 3251.03; 3285.64

VI. N₂ (nitrogen molecule)

Geometry [xyz format, Angstroms]:

N	-1.0710865545	0.0000000000	0.0000000000
N	0.0431865545	0.0000000000	0.0000000000

UCCSD/aug-cc-pVDZ energy [Hartree]: -109.281236323797

Zero point energy [Hartree]: 0.00544991

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:
2392.23

VII. N₂⁺ (nitrogen molecular cation)

Geometry [xyz format, Angstroms]:

N	-1.0790400845	0.0000000000	0.0000000000
N	0.0511400845	0.0000000000	0.0000000000

UCCSD/aug-cc-pVDZ energy [Hartree]: -108.713912213932

Zero point energy [Hartree]: 0.00512180

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:
2248.21

VIII. H (hydrogen atom)

Geometry [xyz format, Angstroms]:

H	0.0000000000	0.0000000000	0.0000000000
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UCCSD/aug-cc-pVDZ energy [Hartree]: -0.49933432

IX. H₂ (hydrogen molecule)

Geometry [xyz format, Angstroms]:

H	1.1008424295	0.0000000000	0.0000000000
H	0.3391575705	0.0000000000	0.0000000000

UCCSD/aug-cc-pVDZ energy [Hartree]: -1.164899490707

Zero point energy [Hartree]: 0.00989769

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:
4344.59

X. c-C₃H₃⁺ (cyclopropenylum cation)

Geometry [xyz format, Angstroms]:

C	0.7976093513	0.0000000000	0.0000000000
C	-0.3988102523	-0.6907667057	0.0000000000
C	-0.3988102523	0.6907667057	0.0000000000
H	1.8898596387	0.0000000000	0.0000000000
H	-0.9449242427	-1.6366645541	0.0000000000

H	-0.9449242427	1.6366645541	0.0000000000
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -115.397494778300</i>			
<i>Zero point energy [Hartree]: 0.04503227</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
741.40; 946.78; 946.84; 973.65; 973.78; 1033.06; 1313.43; 1313.52; 1657.91; 3271.36; 3272.54; 3322.62			
XI. C₃H₃⁺ (propargylium, H2CCCH cation)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	0.0000000000	0.0000000000	-1.2633764250
C	0.0000000000	0.0000000000	0.1004169613
C	0.0000000000	0.0000000000	1.3474978829
H	0.0000000000	0.9482019685	-1.8190593942
H	0.0000000000	-0.9482019685	-1.8190593942
H	0.0000000000	0.0000000000	2.4340803692
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -115.350770609835</i>			
<i>Zero point energy [Hartree]: 0.04196899</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
182.13; 207.57; 544.99; 831.85; 1024.06; 1138.51; 1142.46; 1480.79; 2112.68; 3136.94; 3252.31; 3367.97			
XII. c-C₃H₂⁺ (cyclopropadiene cation)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	-0.7056758857	-0.2907172668	-0.3420045337
C	0.7056362429	-0.2908111804	-0.3419986586
C	0.0000473031	0.7523613549	0.2075860886
H	-1.6224502073	-0.8192085447	-0.6204981362
H	1.6223425468	-0.8194243630	-0.6204847601
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -114.696968780225</i>			
<i>Zero point energy [Hartree]: 0.03269944</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
802.27; 899.70; 958.72; 978.27; 1214.38; 1305.68; 1650.43; 3258.60; 3285.36			
XIII. C₃H₂⁺ (propynylidene cation)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	0.0000000000	0.0001151590	0.0001263495
C	0.0000000000	-0.2577197832	1.2544987467
C	0.0000000000	0.2576801488	-1.2543280263
H	0.0000000000	-0.6118727516	2.2843978686
H	0.0000000000	0.6124810060	-2.2840070821
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -114.676720987715</i>			
<i>Zero point energy [Hartree]: 0.02571275</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
71.25; 223.46; 341.88; 355.29; 784.88; 1296.41; 1905.05; 3331.23; 3332.31			
XIV. C₃H₂⁺ (propadienylidene cation)			
<i>Geometry [xyz format, Angstroms]:</i>			
C	0.0000000000	0.0000000000	-1.2682679040
C	0.0000000000	0.0000000000	0.1013126445
C	0.0000000000	0.0000000000	1.3521880142
H	0.0000000000	0.9506913272	-1.8209385309
H	0.0000000000	-0.9506913272	-1.8209385309
<i>UCCSD/aug-cc-pVDZ energy [Hartree]: -114.626847786201</i>			
<i>Zero point energy [Hartree]: 0.03059799</i>			
<i>UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm⁻¹]:</i>			
188.98; 974.94; 1139.28; 1144.24; 1473.81; 2128.33; 3131.39; 3250.00			
XV. C₃H⁺ (CCCH cation)			

Geometry [xyz format, Angstroms]:

C	2.7341389160	-0.2311493924	0.0000000000
C	3.8160357432	0.3934985786	0.0000000000
C	1.5546909363	-0.9120790234	0.0000000000
H	4.7621344044	0.9397298371	0.0000000000

UCCSD/aug-cc-pVDZ energy [Hartree]: -114.021833877579

Zero point energy [Hartree]: 0.01865464

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:

751.07; 751.49; 1198.55; 2166.64; 3320.69

XVI. $\text{c-C}_3\text{H}^+$ (cyclopropadiene cation)

Geometry [xyz format, Angstroms]:

C	2.8979440960	0.5553392578	0.0000000000
C	2.8516596626	-0.8427653219	0.0000000000
C	1.7103112330	-0.1838378971	0.0000000000
H	3.4480850083	1.5082639612	0.0000000000

UCCSD/aug-cc-pVDZ energy [Hartree]: -113.990428100888

Zero point energy [Hartree]: 0.01863552

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:

835.70; 998.55; 1394.10; 1721.94; 3229.76

XVII. $\text{N}_2\text{C}_3\text{H}_4^+$ (1H-Imidazole cation)

Geometry [xyz format, Angstroms]:

N	0.0000000000	-0.1467094307	-1.2193307642
H	0.0000000000	-1.0257434418	1.9039604483
C	0.0000000000	0.8143699312	0.8732276355
H	0.0000000000	1.5202759791	1.7055901338
C	0.0000000000	1.0278922448	-0.5821545773
H	0.0000000000	1.9908768446	-1.0953800738
H	0.0000000000	-2.1651658712	-0.4113124688
C	0.0000000000	-1.0860752483	-0.2518306432
N	0.0000000000	-0.5171433470	1.0213037734

UCCSD/aug-cc-pVDZ energy [Hartree]: -225.306107281781

Zero point energy [Hartree]: 0.07038407

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:

505.02; 541.20; 722.07; 817.85; 818.20; 877.68; 913.19; 915.69; 965.59; 1049.27; 1124.18; 1202.66; 1257.60; 1289.40; 1441.93; 1467.39; 1550.30; 3271.33; 3279.02; 3284.52; 3600.96

XVIII. $\text{N}_2\text{C}_3\text{H}_4^+$ (pyrazole cation)

Geometry [xyz format, Angstroms]:

N	0.0000000000	1.0167534422	-0.4216733834
N	0.0000000000	-0.0137352323	-1.1615315587
C	0.0000000000	-1.1430716894	-0.2891569868
C	0.0000000000	-0.7234126404	1.0192144841
C	0.0000000000	0.7151176967	0.9752875484
H	0.0000000000	1.9469752544	-0.8536360224
H	0.0000000000	-2.1372044578	-0.7303468965
H	0.0000000000	-1.3287285453	1.9249578449
H	0.0000000000	1.4961476114	1.7357794050

UCCSD/aug-cc-pVDZ energy [Hartree]: -225.264367810707

Zero point energy [Hartree]: 0.06917759

UCCSD/aug-cc-pVDZ harmonic vibrational frequencies [cm^{-1}]:

465.60; 497.63; 544.03; 751.98; 805.86; 853.10; 888.69; 927.19; 941.44; 986.67; 1093.63; 1105.22; 1243.88; 1311.87; 1437.25; 1525.14; 1565.41; 3285.60; 3297.13; 3317.29; 3520.85