

HCN elimination from vinyl cyanide: Product energy partitioning, the role of hydrogen-deuterium exchange reactions and a new pathway

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SUPPORTING INFORMATION

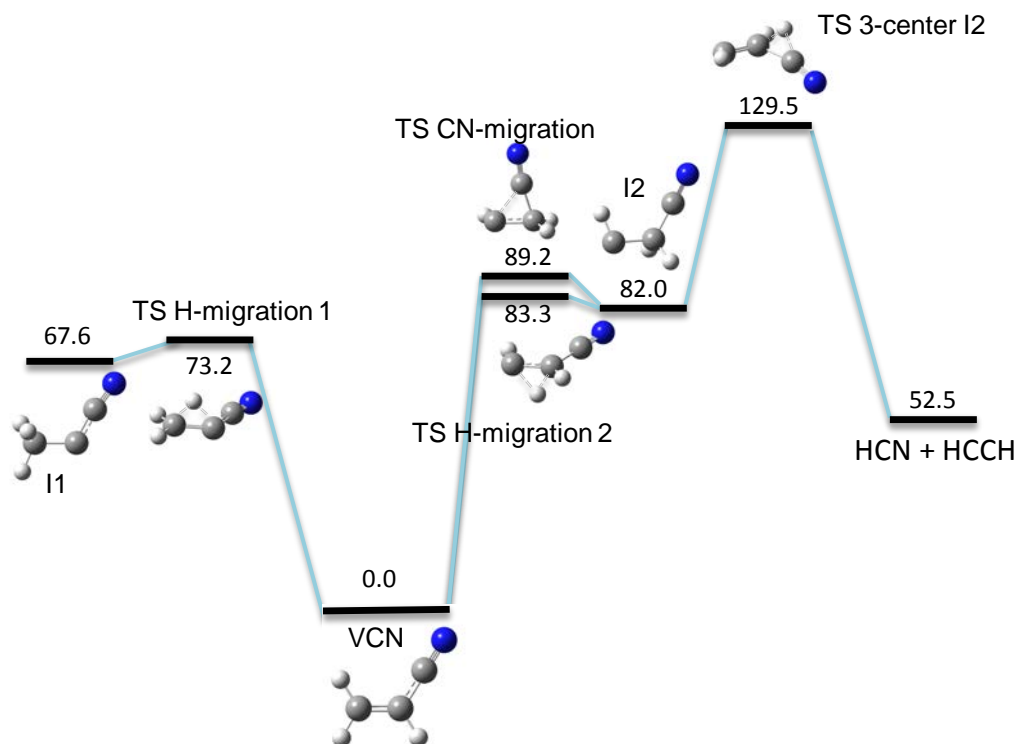


Figure 1S. Different H- and CN-migration channels considered in the KMC simulations from singly deuterated VCN. The relative energies are calculated at the MPWB1K/6-31+G(d,p) level of theory. The energies do not include the zero-point energy correction because that depends on the position of the hydrogens and deuteriums in the molecule.

For the KMC simulations that start from singly deuterated VCN ($\text{CH}_2=\text{CD-CN}$), besides the pathways of Figure 1 of the manuscript, the H- and CN- migration channels shown in Figure 1S are considered.

For the TS “H-migration 2” channels of Figure 1S there are two transition states: TS “H-migration 2 cis” and and TS “H-migration 2 trans” (see below), but, for clarity, only one has been depicted in the figure. The four HCN elimination paths of Figure 1 of the manuscript involve eight elementary steps, and the five H- and CN- migration paths of

Figure 1S (including the additional HCN elimination channel TS 3-center I2) involve nine elementary steps, which makes a total of 17 elementary steps.

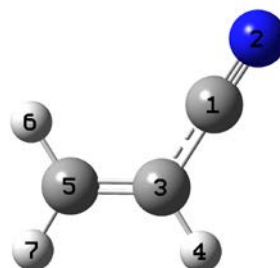
Although the HCN elimination pathway involving TS “3-center I2” of Figure 1S is new, this is a minor channel. In fact, the KMC simulations indicate that the amount of HCN produced via this pathway at 193 nm is negligible (~0.1%).

Since deuterium can occupy any of the three different positions in VCN, a total of $17 \times 3 = 51$ elementary steps are considered in this set of KMC simulations. The electronic energies, optimized geometries (Cartesian coordinates in Å), and vibrational frequencies (in cm^{-1}) obtained at the MPWB1K/6-31+G(d,p) level for all the stationary points (which is the input of the RRKM calculations) are collected below.

VCN

-170.745958 au

C	-0.575731	-0.525879	0.000000
N	-1.062613	-1.569455	0.000000
C	0.002923	0.776836	0.000000
H	-0.693083	1.602004	0.000000
C	1.315291	0.973890	0.000000
H	2.011233	0.150245	0.000000
H	1.718240	1.973606	0.000000



Frequencies (the number after D indicates the position of deuterium):

D4	D6	D7
238	230	234
347	349	333
578	559	578
710	699	651
881	866	802
902	877	928
933	1034	1028
1029	1055	1080
1208	1262	1335
1467	1403	1345
1734	1721	1723
2422	2437	2439

2453	2448	2448
3253	3280	3282
3355	3312	3306

HCCH

-77.285279 au

C	0.000000	0.000000	0.599188
C	0.000000	0.000000	-0.599188
H	0.000000	0.000000	1.660353
H	0.000000	0.000000	-1.660353

HCN

-93.377052 au

N	0.000000	0.000000	0.647924
C	0.000000	0.000000	-0.498203
H	0.000000	0.000000	-1.562565

H₂CC:

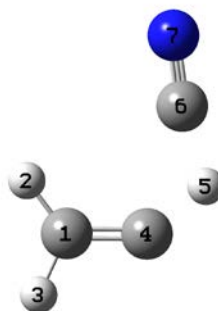
-77.218706 au

C	0.000000	0.000000	-0.477153
C	0.000000	0.000000	0.815017
H	0.000000	0.936566	-1.021120
H	0.000000	-0.936566	-1.021120

TS 3-center

-170.564986 au

C	-0.051538	-1.706421	0.000000
H	-1.103567	-1.478545	0.000000
H	0.253062	-2.746672	0.000000
C	0.945979	-0.874489	0.000000
H	1.170438	0.321228	0.000000
C	0.026669	1.051440	0.000000
N	-0.832199	1.822527	0.000000



Frequencies:

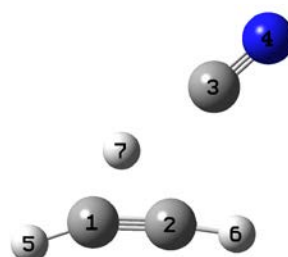
D2	D3	D5
-1362	-1363	-1041
130	131	133
182	186	189
281	283	281
478	481	522
537	496	577
832	812	663

848	879	930
891	887	935
1213	1223	1337
1656	1666	1502
2242	2253	1865
2389	2383	2371
2472	2392	3222
3247	3327	3346

TS 4-center

-170.541784 au

C	-1.125923	1.521978	0.000000
C	-1.237378	0.293939	0.000000
C	0.922992	-0.537082	0.000000
N	1.645614	-1.447397	0.000000
H	-1.407809	2.550593	0.000000
H	-1.457652	-0.750469	0.000000
H	-0.006623	0.997765	0.000000



Frequencies:

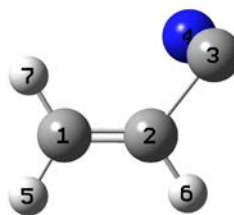
D5	D6	D7
-1659	-1666	-1281
69	69	70
119	120	119
304	305	300
413	415	418
553	565	532
573	673	723
707	688	723
769	767	748
926	791	921
1846	1848	1500
2066	2069	1943
2296	2296	2295
2651	2649	3434
3476	3479	3514

TS iso

-170.652717

C	1.410178	-0.259249	0.081802
C	0.342563	0.506355	-0.083450

C	-1.088891	0.207625	0.550964
N	-1.135567	-0.444793	-0.440816
H	2.384682	0.117268	-0.186119
H	0.375681	1.483842	-0.532587
H	1.337773	-1.251360	0.495346



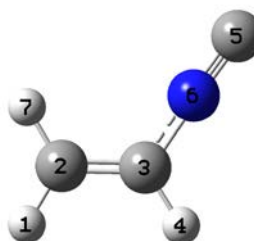
Frequencies:

D5	D6	D7
-391	-391	-393
248	243	238
417	429	398
513	583	558
725	773	764
901	866	875
953	899	956
1035	989	1027
1293	1137	1256
1333	1422	1350
1667	1682	1665
2079	2078	2079
2432	2459	2446
3317	3255	3298
3320	3358	3324

VisoCN

-170.715268 au

H	1.719232	1.887389	0.000000
C	1.313054	0.890313	0.000000
C	0.001543	0.714929	0.000000
H	-0.696902	1.537098	0.000000
C	-1.127567	-1.559039	0.000000
N	-0.584092	-0.525078	0.000000
H	1.993230	0.054520	0.000000



Frequencies:

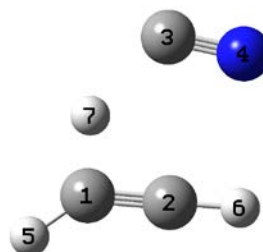
D1	D4	D7
221	223	218
289	295	297
522	532	497
627	718	695
814	865	858

914	928	883
1009	966	1011
1127	987	1088
1320	1204	1281
1366	1450	1404
1735	1740	1733
2302	2302	2303
2450	2436	2444
3291	3262	3288
3313	3366	3326

TS 5-center

-170.545947

C	-1.187165	1.027139	0.000000
C	-1.129428	-0.218388	0.000000
C	1.343543	0.129621	0.000000
N	1.242242	-1.036064	0.000000
H	-1.911176	1.818421	0.000000
H	-1.072825	-1.284844	0.000000
H	0.015580	1.144969	0.000000



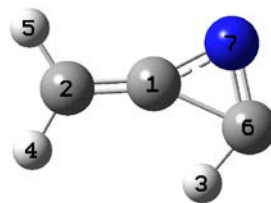
Frequencies:

D5	D6	D7
-1380	-1397	-1099
133	132	137
269	268	268
361	359	360
411	374	407
509	574	559
690	646	731
731	730	817
902	916	862
940	965	889
1766	1753	1317
1817	1814	1854
2238	2237	2235
2556	2640	3383
3482	3395	3490

TS cyc

-170.592582

C	-0.176171	-0.000010	0.003876
C	-0.031337	-0.000014	1.308549
H	1.286627	0.000010	-0.822763
H	0.935911	-0.000005	1.781518
H	-0.912087	-0.000027	1.932622
C	0.395661	0.000003	-1.482893
N	-0.861340	-0.000013	-1.138738



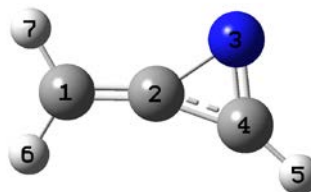
Frequencies:

D3	D4	D5
-661	-852	-852
325	316	316
433	434	418
563	533	549
689	725	698
782	766	770
832	863	885
1001	887	910
1056	1034	1003
1463	1333	1351
1524	1529	1530
1924	1919	1923
2273	2435	2411
3238	3085	3085
3338	3278	3304

cyc

-170.676763

C	-0.024647	-0.000014	1.238226
C	-0.052205	-0.000008	-0.076057
N	-0.898650	-0.000013	-1.227866
C	0.358714	0.000002	-1.401336
H	1.056841	0.000014	-2.221244
H	0.914514	-0.000005	1.764513
H	-0.941440	-0.000027	1.803654



Frequencies:

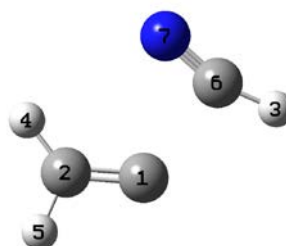
D5	D6	D7
358	348	345
432	451	438
708	590	614
744	792	798
744	808	829
840	872	872

879	934	883
1045	996	999
1157	1194	1226
1480	1366	1350
1666	1690	1690
1938	1963	1963
2510	2439	2434
3254	3305	3310
3354	3327	3327

TS CCdiss

-170.592482

C	-0.235786	0.001634	0.053193
C	0.025319	-0.000129	1.329229
H	0.591786	-0.001017	-2.319022
H	0.968001	-0.004623	1.846433
H	-0.891962	0.003747	1.910695
C	1.152464	-0.003964	-1.411906
N	2.036647	-0.008302	-0.659110



Frequencies:

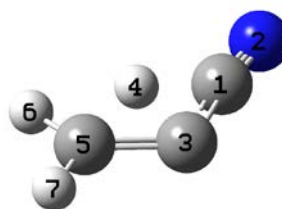
D3	D4	D5
-365	-365	-363
105	106	111
247	240	244
384	364	376
532	470	422
653	663	631
653	782	808
758	810	819
871	907	913
1314	1166	1179
1736	1697	1714
2011	2184	2184
2740	2474	2366
3205	3225	3340
3353	3496	3496

TS H-migration 1

-170.629308 au

C	0.000000	0.000000	0.000000
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N	0.000000	0.000000	1.156859
C	0.159779	0.000000	-1.405985
H	-0.635573	-0.899798	-1.966858
C	-0.975572	0.299288	-2.141297
H	-1.922717	0.629828	-1.719786
H	-0.900114	0.320629	-3.221030



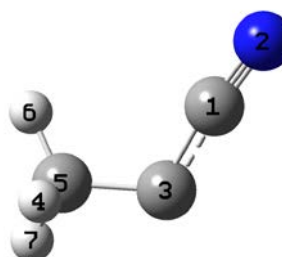
Frequencies:

D4	D6	D7
-700	-899	-884
233	222	226
300	307	298
597	582	594
689	728	688
909	891	832
1039	940	1044
1150	1006	1074
1187	1313	1246
1441	1423	1354
1553	1509	1516
1711	2275	2302
2367	2358	2365
3146	2370	2388
3267	3247	3174

II

-170.638281 au

C	0.269922	-0.050653	0.640121
N	0.266033	-0.064588	1.804959
C	0.446157	-0.038249	-0.736332
H	-1.040514	-0.915502	-1.663667
C	-0.751401	0.143961	-1.539902
H	-1.604908	0.650658	-1.090996
H	-0.540089	0.494969	-2.544350



Frequencies:

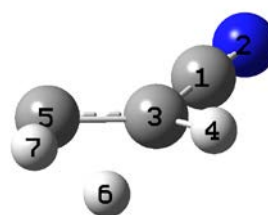
D4	D6	D7
177	197	166
221	210	213
362	371	360
528	579	524
607	633	601

904	900	819
1088	947	988
1232	1156	1035
1255	1294	1231
1295	1383	1259
1540	1413	1407
2206	2251	2197
2253	2304	2253
3128	3022	2360
3224	3209	3149

TS H-migration 2 cis

-170.610403 au

C	0.775805	0.057286	-0.001076
N	1.897301	-0.192354	-0.019512
C	-0.621845	0.437240	-0.016645
H	-0.756361	1.512398	-0.138806
C	-1.636806	-0.522658	-0.087946
H	-1.055057	-0.041025	1.036460
H	-2.572608	0.043893	-0.127065



Frequencies:

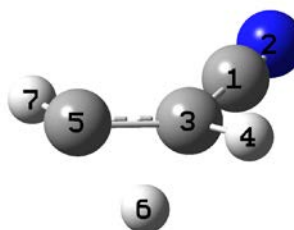
D4	D6	D7
-757	-587	-758
247	250	244
328	325	318
596	604	594
821	807	733
893	893	792
958	1005	1052
987	1133	1072
1238	1190	1220
1266	1317	1317
1443	1459	1468
2277	1710	2283
2356	2465	2331
2466	3111	2465
3118	3146	3140

TS H-migration 2 trans

-170.613184 au

C	0.761418	0.101301	-0.011495
N	1.863043	-0.227921	0.005095

C	-0.638328	0.482733	-0.038048
H	-0.798690	1.538995	-0.228432
C	-1.731945	-0.397052	-0.094801
H	-1.247846	0.342872	0.994863
H	-1.341630	-1.408315	0.063965



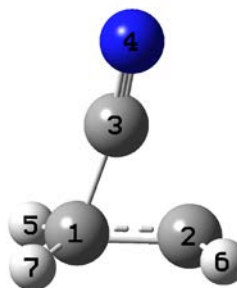
Frequencies:

D4	D6	D7
-627	-503	-645
230	233	223
322	310	320
590	596	568
781	723	749
891	914	856
961	1003	923
1047	1148	1021
1204	1211	1252
1249	1351	1392
1401	1435	1451
2356	1767	2286
2413	2452	2407
2453	3112	2452
3112	3211	3211

TS CN-migration

-170.6038815

C	0.920891	-0.601453	0.039221
C	0.972083	0.828256	-0.181203
C	-0.508896	-0.127410	-0.050993
N	-1.647638	0.058651	0.029684
H	1.079900	-1.231165	-0.830882
H	1.020329	1.325440	0.794961
H	1.128775	-1.101191	0.985990



Frequencies:

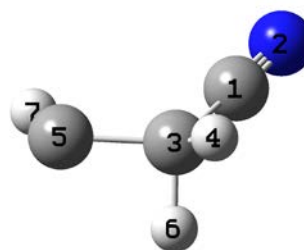
D5	D6	D7
-449	-452	-450
255	251	260
374	376	362
733	643	691
787	748	801

806	770	813
934	1071	982
1121	1150	1111
1204	1177	1173
1217	1225	1256
1414	1543	1413
2341	2279	2295
2349	2346	2349
3098	3112	3101
3139	3214	3197

I2

-170.615222 au

C	0.006761	0.003815	0.006854
N	-0.030949	0.006827	1.155907
C	0.111319	-0.004138	-1.447310
H	-0.662395	-0.689911	-1.862555
C	1.182553	-0.718486	-2.135518
H	1.588848	-1.448736	-1.418872
H	-0.139293	0.962165	-1.877274



Frequencies:

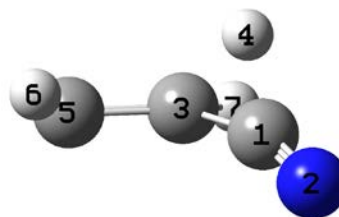
D4	D6	D7
217	212	219
296	321	307
350	347	383
566	545	564
687	625	702
820	850	886
915	994	922
1139	1037	1037
1215	1215	1166
1244	1326	1230
1394	1407	1294
2156	2252	2339
2457	2457	2457
3065	2945	2950
3186	3188	3065

TS 3-center I2

-170.539639 au

C	0.000000	0.000000	0.000000
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N	0.000000	0.000000	1.169090
C	0.458236	0.000000	-1.531590
H	-0.809419	-0.134232	-0.928234
C	0.987564	-1.122278	-2.042003
H	0.698789	-2.053817	-1.559096
H	0.431118	1.015371	-1.887020



Frequencies:

D4	D6	D7
-1115	-1315	-1326
199	193	200
407	397	390
515	515	531
563	577	623
621	659	626
837	749	887
948	864	911
1023	1050	970
1287	1313	1060
1441	1473	1470
1640	2101	2100
2262	2343	2346
3231	2392	2454
3311	3311	3231