Supporting material (ESI) for PCCP

Dissociative Ionisation of Adamantane: A Combined Theoretical and Experimental Study

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C_3H_6 and C_3H_7-loss

Fig. S1 shows potential energy surface for the C_3H_6 and C_3H_7-loss of the adamantane cation derived from quantum chemical calculations. The steps up to **int2** are described in the main paper. For both decomposition reactions, we could identify two pathways yielding either $C_7H_{10}^+$ or $C_7H_9^+$ as presented in Fig. S3 and S4, respectively.

In the first pathway resulting in the loss of C_3H_6, H21 is shifted from C4 to C3 (**ts3 -> int3**) causing the C1-C2 bond to break. The resulting **int3** can be described as a 6-membered ring substituted with both a methyl and allyl group. The following steps are the concerted breaking of the C8-C7 bond and elongation of the C12-H14 bond (**ts4**) toward C7, with the production of propene (C_3H_6) and 3-methyl-1,4-cyclohexadiene cation $C_7H_{10}^+$ (**P1-1**). Along the second C_3H_6-loss path, C1-C2 bond cleavage (**int5**) is caused by shifting of H21 from C3 to C2 (**ts5**) and to C1 creating a terminal methyl group (**ts6-> int6**). Eventually, moving H13 from C12 to C4 causes the breaking of the C7-C8 bond and the release of propene (**P1-2**).

The C_3H_7 loss of follows the same initial steps as the C_3H_6 loss, up to **int5**. However a branching occurs leading to a hydrogen transfer (H14) from C12 to C6 creating a lose chain, with a radical site at C1, which establishes a bond with another radical site at C3 (**int8**), leading to a bridged 6-membered ring. After another hydrogen transfer of H10 towards C7 the C7-C8 bond breaks and a methyl, propyl-substituted cyclohexenyl is formed (**int 9**). Two consecutive H scrambling –H21 from C2 to C9 (**ts10 and int10**) and H18 from C16 to C1 (**ts11**) – allow the release of an isopropyl unit and the formation of **P2-2**. The second route branches at the quite stable intermediate **int9** (0.49 eV lower in energy than the adamantane cation) and through a single transition state, where H21 is shifting from C2 to C3 (**ts12**), permitting the release of propyl radical and formation of 1-methyl cyclohexa-1,3-diene cation (**P2-1**, Fig. S4). The barrier for **ts12** is 0.35 eV higher than the limiting barrier at **ts2**, thus the other pathway likely dominates.

C_4H_8-loss

Three possible routes were identified for the release of the C_4H_8 fragments, which are depicted in Fig. S2. Intermediate and transitions state structure can be found in Fig.5 and Fig.6. All routes share the same steps up to **int14**: H25 migrates from C1 to C6 (**ts13 -> int13**) and the C3-C2 bond is broken, creating a C_4H_7 group attached to a 6-membered carbon ring (**int14**, Fig. S5). The first route proceeds through **int15** were H11 moves from C9 in the ring to C3 and eventually a C_4H_8 group is release (**P3-1**, Fig. S5).

The second route is more complex, requiring several hydrogen shifts (Fig. S2). Starting from **int15**, it undergoes a two-step hydrogen-alkyl exchange between C4 and C12 (**ts17 ->int17->ts18->int18**), followed by a hydrogen transfer (H20 from C4 to C5, **int19**). At this point H15 shifts from C8 (on the ring) to C5, creating a structure (**int20**) which is ~0.7 eV more stable than the adamantane cation. From there, surpassing a barrier of ~3 eV (**ts21**), H21 moves from C3 to C8, causing the breaking of the C8-C12 bond and the release of the C_4H_8 group in the form of 1-butene (**P3-2**, Fig. S6).

Along the third route, after **int14**, we have again a series of hydrogen shifts; first H18 moves from C6 to C1 (**int24**), then H16 moves from C7 to C6 (**int25**) and the final jump of H11 from C9 to C3 triggers the release of an isobutene unit (**P3-1**, Fig. S5), resulting in the same product as for the first pathway.

C_2H_4 and CH_3-loss

Only one pathway was found for each species that could occur at energies relevant to those described in the experimental section. These processes appear parallel to the C_4H_8-loss reactions (Fig. S2). After formation of the quite stable intermediate **int20**, the C4-C5 bond is broken and a new bond is formed between C4 and C8, triggering the methyl loss (Fig. S6). This process is quite endoergic; it requires 2.71 eV to overcome **ts23** and it is 0.45 eV above the common limiting transition state. The ethylene loss occurs after shifting H15 from C8 to C9 in intermediate **int19** (Fig S6), with an additional barrier of 0.5 eV (**ts22**, Fig. S6).

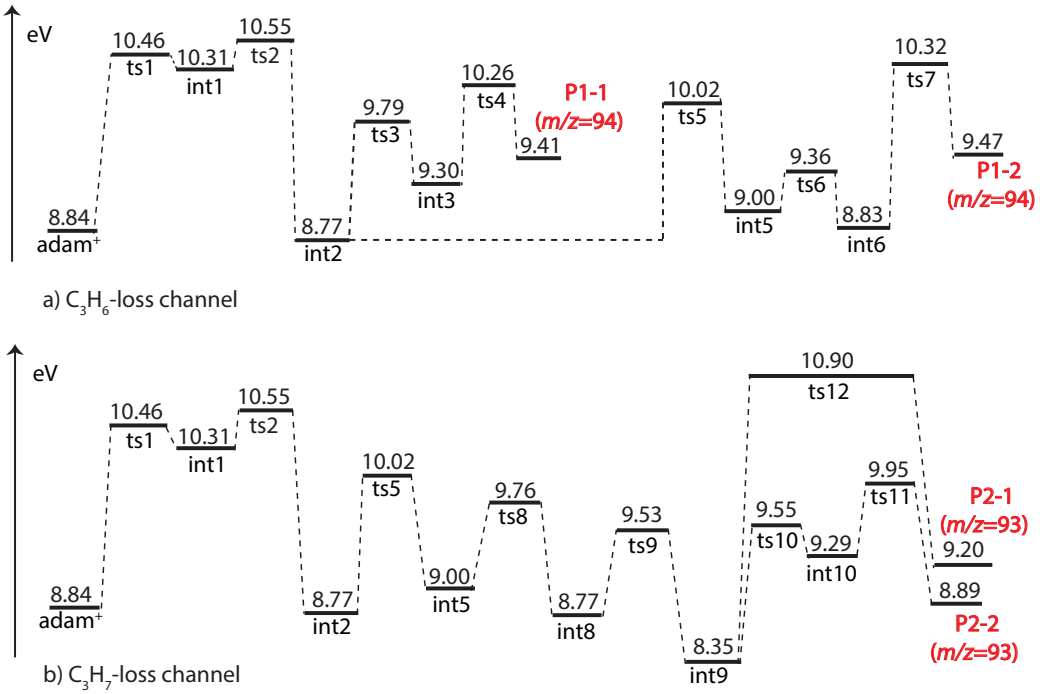

Figure S1: Potential Energy Surface for the most probable channels leading to C_3H_6 (m/z=94) and C_3H_7 (m/z=93). Structures are represented in Fig. S3 and S4 of this ESI. Energies are in eV with respect to adamantane.

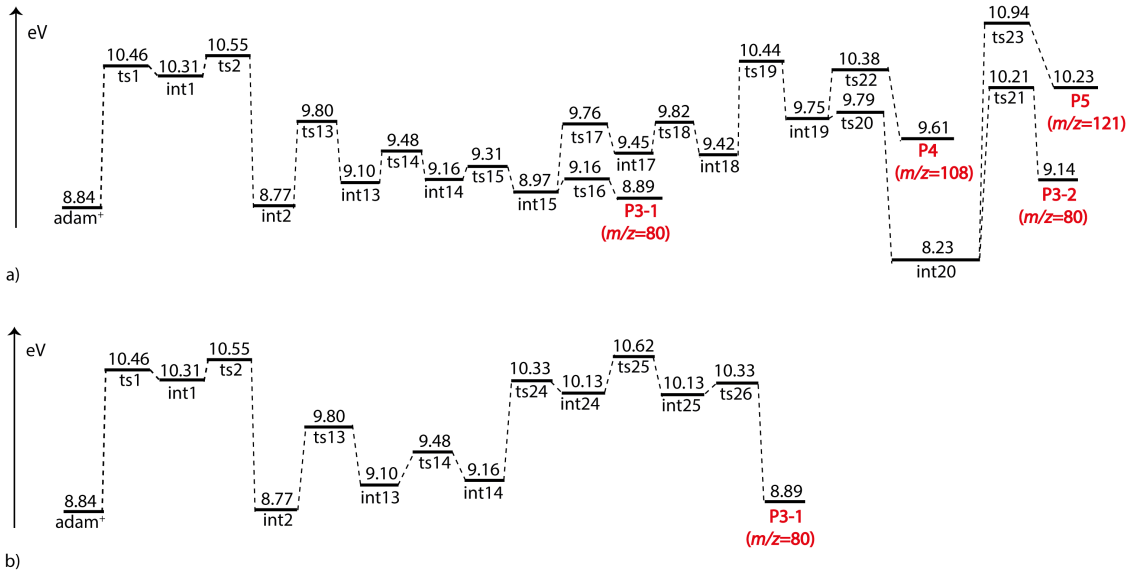

Figure S2: as above but for C_4H_8 (m/z=80) (a,b), C_2H_4 (m/z=108) and CH_3 (m/z=121) channels (b). Structures are represented in Fig. S5 and S6 of this ESI.

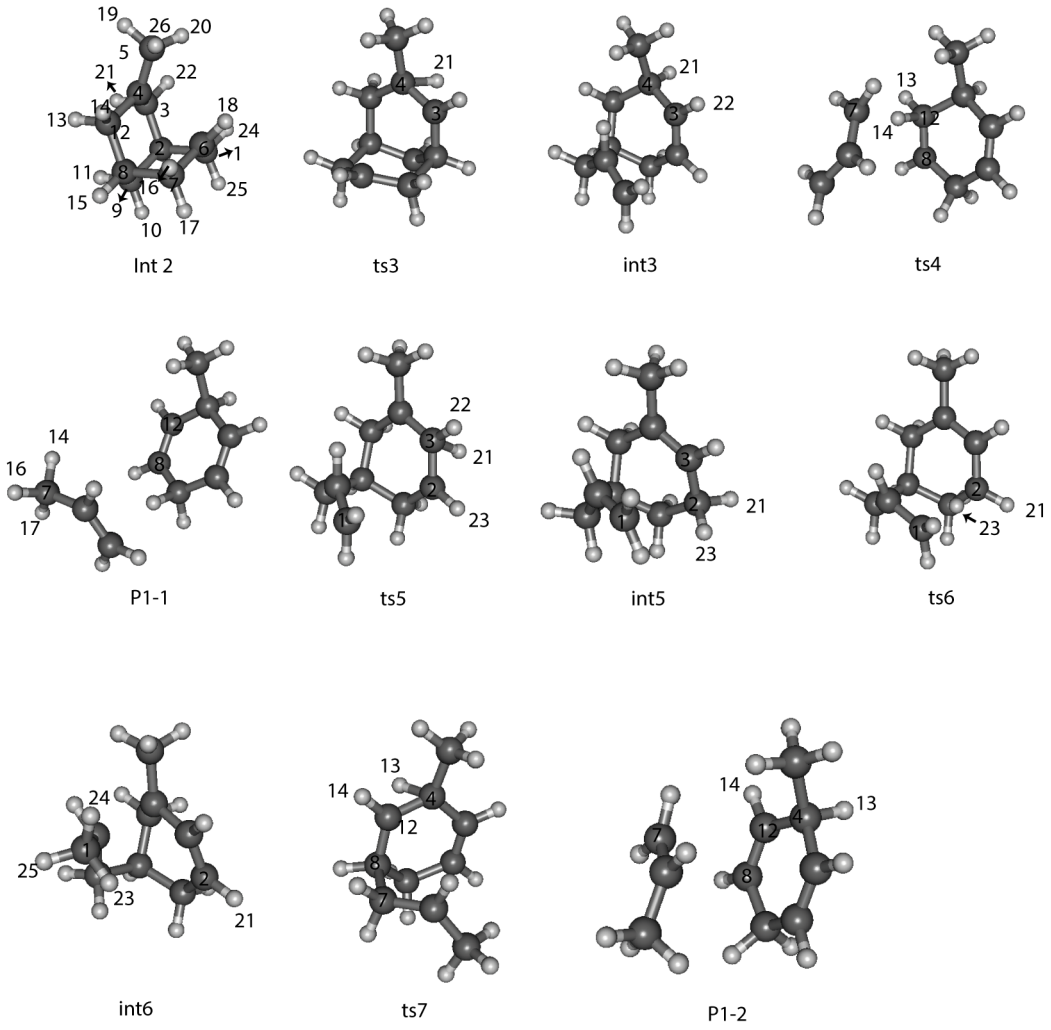

Figure S3: Molecular structures for transition and intermediate states leading to C_3H_6 loss. Atoms are numbered to help following structural changes.

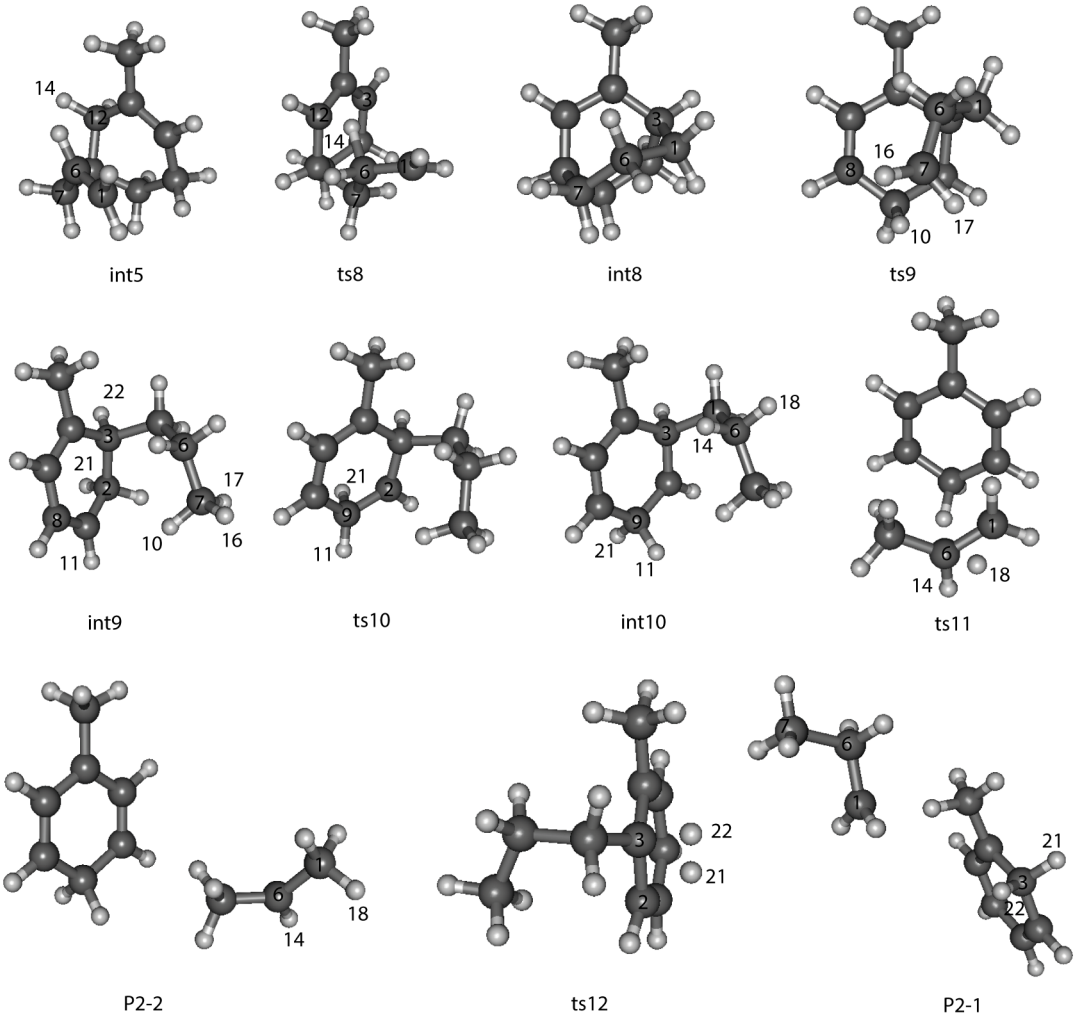

Figure S4: Molecular structures for transition and intermediate states leading to C_3H_7 loss. Atoms are numbered to help following structural changes.

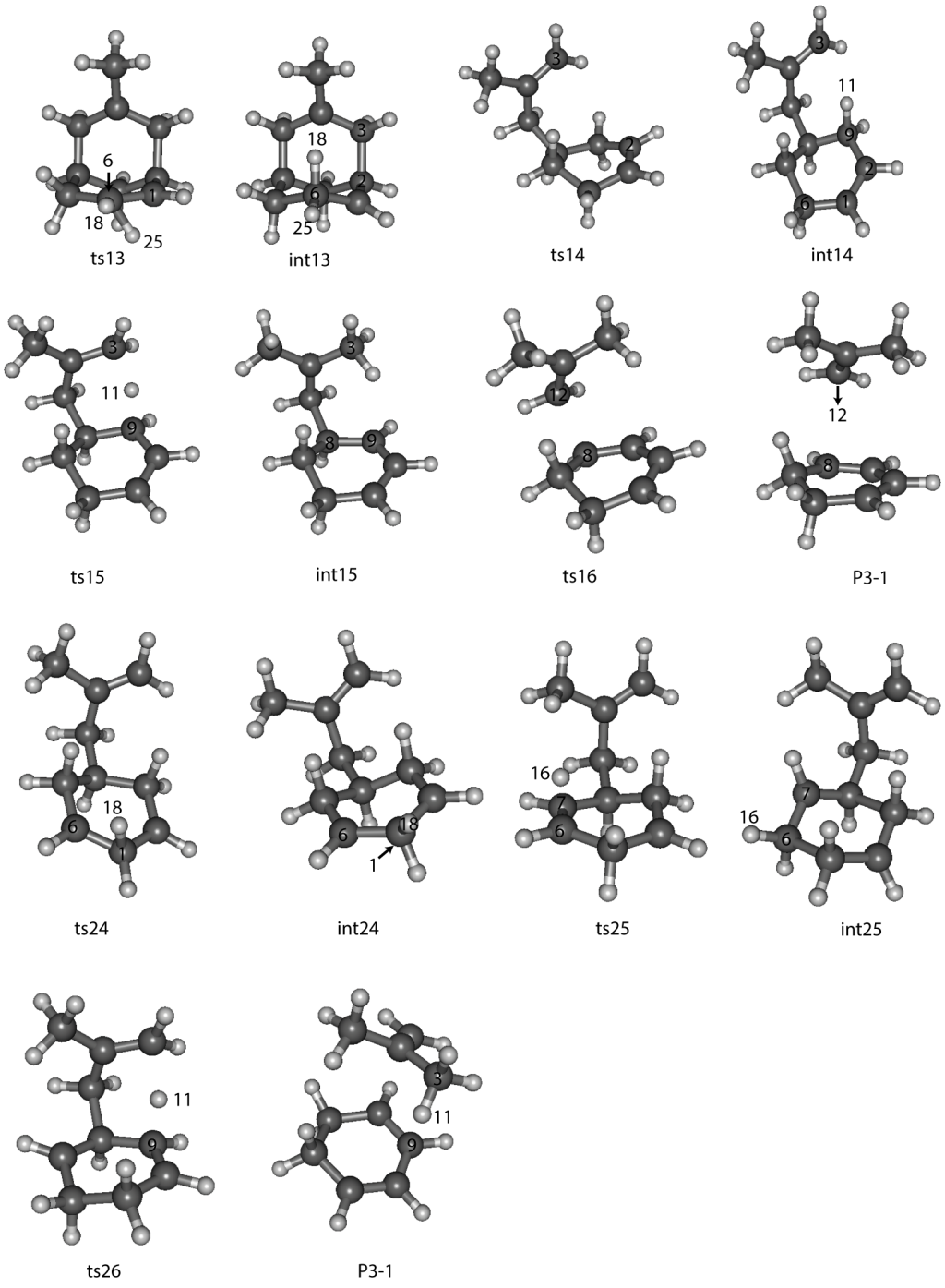

Figure S5: Molecular structures for transition and intermediate states leading to C_4H_8 loss. Atoms are numbered to help following structural changes.

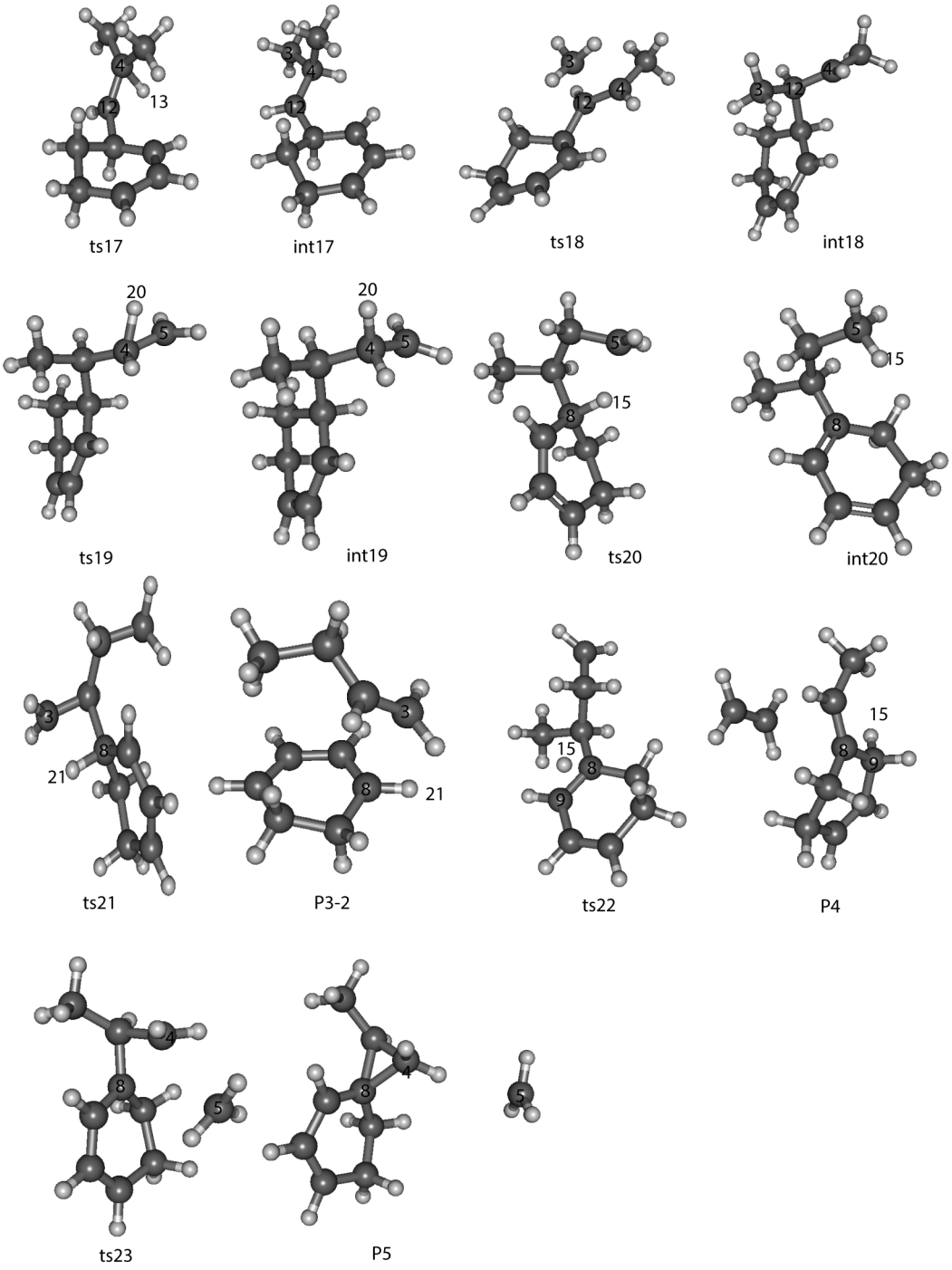

Figure S6: Molecular structures for transition and intermediate states leading to C_4H_8 , C_2H_4 and CH_3 loss. Atoms are numbered to help following structural changes.

B3LYP/6-311++G(2d,p) optimized structure of transition state TS2.

6	1.319480	-1.307854	-0.592356
6	0.475779	-1.272223	0.692662
6	-1.049901	-1.324158	0.422038
6	-1.576027	-0.031452	-0.201349
6	-2.106557	-0.027787	-1.526588
6	1.615778	0.001835	-1.199642
6	1.297325	1.298709	-0.576278
6	0.454486	1.232894	0.708114
6	0.819476	-0.021669	1.513553
1	1.886422	-0.014079	1.753323
1	0.285073	-0.032092	2.466928
6	-1.071885	1.262221	0.437992
1	-1.569591	1.391458	1.402549
1	-1.342006	2.123198	-0.177465
1	0.670581	2.124665	1.299668
1	0.847454	1.970438	-1.325444
1	2.251384	1.803111	-0.343405
1	2.124222	0.012070	-2.158253
1	-2.380931	-0.957137	-2.013639
1	-2.396739	0.902701	-2.002167
1	-2.739375	-0.042370	-0.034390
1	-1.545237	-1.473723	1.384876
1	-1.305413	-2.181944	-0.204020
1	0.707063	-2.167422	1.273194
1	0.881013	-1.977841	-1.349798
1	2.281999	-1.798801	-0.365623

B3LYP/6-311++G(2d,p) optimized structure of transition state TS4

6	2.331398	2.435408	-0.082567
6	-0.100487	-1.787054	-1.787660
6	-1.275857	-1.561403	-1.210391
6	-1.443275	-1.312496	0.269299
6	-2.648718	-0.420301	0.587357
6	1.016340	2.288077	-0.406804
6	0.017676	2.038006	0.554331
6	1.082317	-1.289563	0.351778
6	1.185079	-1.829059	-1.011322
1	2.011274	-1.326053	-1.536839
1	1.564323	-2.864675	-0.919245
6	-0.132200	-0.807038	0.887054
1	-0.144066	-0.712882	1.974383
1	-0.005536	0.388008	0.583730
1	1.995107	-1.197592	0.934413
1	-1.027021	2.138393	0.289746
1	0.258422	2.117443	1.609588
1	0.718400	2.355160	-1.448317

1	-2.601982	0.529802	0.051803
1	-2.723897	-0.215203	1.657265
1	-1.632059	-2.280980	0.754677
1	-2.180599	-1.577490	-1.808344
1	-0.035667	-1.980206	-2.851731
1	3.078990	2.644313	-0.837146
1	2.667520	2.384701	0.947330
1	-3.570169	-0.918193	0.283054

B3LYP/6-311++G(2d,p) optimized structure of transition state TS5

6	1.562196	2.321862	-0.885100
6	0.654508	-0.874995	-1.365186
6	-0.765250	-0.679091	-1.317074
6	-1.463378	-0.555189	-0.072578
6	-2.914791	-0.252830	-0.038498
6	0.742710	1.837066	0.045581
6	1.176952	1.001451	1.216001
6	0.811287	-0.502387	1.128886
6	1.430413	-1.151068	-0.126580
1	2.456978	-0.813765	-0.287416
1	1.511803	-2.238552	0.005535
6	-0.709125	-0.781169	1.197506
1	-0.866927	-1.830618	1.492452
1	-1.168567	-0.197540	2.000164
1	1.261191	-0.982018	2.000047
1	0.741849	1.403042	2.136960
1	2.261763	1.075798	1.329030
1	-0.316971	2.075473	-0.023599
1	-3.449124	-0.991286	0.570869
1	-3.366343	-0.223273	-1.029680
1	-0.451101	-1.842112	-1.516839
1	-1.267457	-0.388046	-2.235448
1	1.131339	-0.882904	-2.338781
1	1.197366	2.935711	-1.699712
1	2.634464	2.159380	-0.841231
1	-3.090648	0.713963	0.450004

B3LYP/6-311++G(2d,p) optimized structure of transition state TS7

6	0.812788	2.621468	1.208944
6	-0.685001	-0.657916	1.510533
6	0.257847	-1.470816	1.034652
6	0.450805	-1.651577	-0.427265
6	1.624469	-2.479399	-0.906824
6	0.920818	1.917239	-0.091620
6	-0.207286	1.697568	-1.002145

6	-1.091543	0.308138	-0.814160
6	-1.618630	0.109449	0.617822
1	-1.855829	1.078992	1.061015
1	-2.574719	-0.428741	0.579963
6	-0.220837	-0.753176	-1.295525
1	-0.557618	-2.172259	-0.876823
1	-0.039808	-0.853161	-2.362892
1	-1.914661	0.469999	-1.510565
1	0.099976	1.722387	-2.049880
1	-0.979496	2.458181	-0.863821
1	1.887412	1.503139	-0.361488
1	1.638380	-3.452347	-0.416028
1	2.547132	-1.959515	-0.638041
1	-0.827931	-0.567945	2.581307
1	0.893490	-2.052651	1.689452
1	-0.115349	3.188838	1.300566
1	0.866677	1.921703	2.056658
1	1.650183	3.312339	1.349070
1	1.613193	-2.626087	-1.986746

B3LYP/6-311++G(2d,p) optimized structure of transition state TS13

6	0.767259	0.883028	-1.375610
6	0.771683	-0.591378	-1.369822
6	-0.764670	-0.991572	-1.369776
6	-1.445449	-0.719006	-0.074987
6	-2.916444	-0.486902	-0.048346
6	0.823731	1.611917	-0.177628
6	0.926135	0.953158	1.175542
6	0.779805	-0.582533	1.144377
6	1.453866	-1.154270	-0.112970
1	2.522526	-0.917559	-0.129882
1	1.376873	-2.243138	-0.122485
6	-0.701058	-1.024088	1.184892
1	-0.714407	-2.111008	1.371777
1	-1.205978	-0.574725	2.044314
1	1.277496	-0.980458	2.029919
1	0.155255	1.408557	1.804122
1	1.875161	1.250353	1.633922
1	0.654115	2.685433	-0.225323
1	-3.267215	0.041621	-0.938094
1	-3.222361	0.076906	0.836192
1	-0.748830	-2.068844	-1.593334
1	-1.291945	-0.523052	-2.205558
1	1.218317	-0.973862	-2.287849
1	0.648181	1.431541	-2.306891
1	1.903217	1.480254	-0.809774
1	-3.469404	-1.438652	-0.013478

B3LYP/6-311++G(2d,p) optimized structure of transition state TS19

6	2.899723	-0.002388	-0.520136
6	2.007189	0.855844	-1.127949
6	-1.276878	1.495765	1.323658
6	-2.367266	0.099946	-0.461454
6	-3.043384	-1.075779	-0.840759
6	2.439850	-1.060947	0.424154
6	1.070479	-0.739233	1.033794
6	0.055009	-0.297475	-0.037774
6	0.638230	0.741016	-0.933285
1	-0.019368	1.393913	-1.496589
1	-2.227890	1.712151	1.814732
6	-1.319966	0.138091	0.612863
1	-2.447621	0.947657	-1.138760
1	-1.555256	-0.644205	1.341682
1	-0.192176	-1.185008	-0.649114
1	1.196642	0.067830	1.759930
1	0.687306	-1.605169	1.578031
1	3.176793	-1.203010	1.219173
1	-3.692157	-1.089318	-1.709179
1	-3.511279	-0.013980	0.003003
1	-0.504738	1.505672	2.091673
1	-1.064676	2.307841	0.625894
1	2.377593	1.614749	-1.807353
1	3.956170	0.067393	-0.750847
1	2.413709	-2.020517	-0.114976
1	-2.990438	-1.963956	-0.220137

B3LYP/6-311++G(2d,p) optimized structure of transition state TS23

6	-2.824336	-0.129976	-0.508224
6	-2.022140	0.991515	-0.548249
6	3.115204	2.015793	-0.408355
6	2.052568	-0.141284	-0.261995
6	1.556535	-0.079039	-1.517210
6	-2.418882	-1.372114	0.188416
6	-0.902929	-1.486506	0.386178
6	-0.289998	-0.162842	0.882860
6	-0.808885	1.007611	0.125276
1	-0.259781	1.941982	0.185669
1	3.833708	1.809912	-1.188412
6	1.248867	-0.178275	1.012798
1	1.554091	0.660495	1.646207
1	1.539451	-1.073125	1.572367
1	-0.652693	0.000372	1.914370
1	-0.442965	-1.777592	-0.560703
1	-0.679287	-2.281621	1.098606

1	-2.821949	-2.243965	-0.334315
1	0.496547	-0.026092	-1.727135
1	3.101330	-0.398397	-0.142106
1	2.274151	2.648995	-0.648388
1	3.448162	1.965556	0.618744
1	-2.368096	1.886004	-1.051746
1	-3.811105	-0.090187	-0.958219
1	-2.938768	-1.370908	1.162323
1	2.216081	-0.072735	-2.375607