

Supplementary Information for

A Chemical Dynamics Study on the Gas Phase Formation of Triplet and Singlet C₅H₂ Carbenes

Chao He^{a†}, Galiya R. Galimova^{b,c†}, Yuheng Luo^{a†}, Long Zhao^a, André K. Eckhardt^d, Rui Sun^{a*},
Alexander M. Mebel^{b*}, Ralf I. Kaiser^{a*}

^a Department of Chemistry, University of Hawai'i at Manoa, Honolulu, Hawaii 96822, USA

^b Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

^c Samara National Research University, Samara 443086, Russia

^d Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

Correspondence to: Prof. Dr. Ralf I. Kaiser: ralfk@hawaii.edu, Prof. Dr. Alexander M. Mebel: mebela@fiu.edu, and Prof. Dr. Rui Sun: ruisun@hawaii.edu

[†]These authors contributed equally to this work.

This PDF file includes:

Figures S1 to S3
Tables S1 to S3

Other supplementary materials for this manuscript include the following:

Movies S1 to S8
Dataset S1

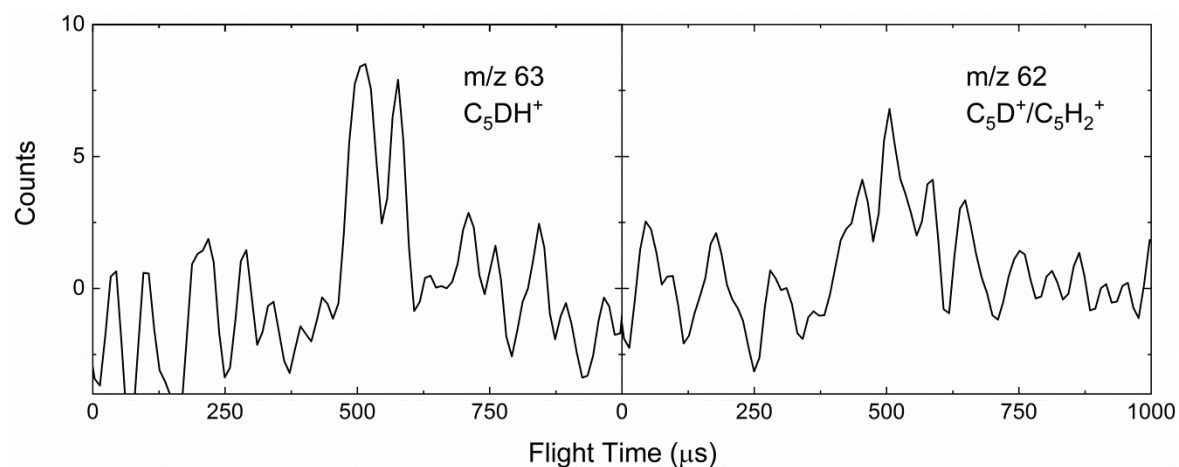


Figure S1. Time-of-flight (TOF) spectra for the reaction of the methylidyne-*d* radical (CD ; $C_{\infty v}$; $X^2\Pi$) with diacetylene ($HCCCCH$; $D_{\infty h}$; $X^1\Sigma_g^+$) recorded at mass-to-charge (m/z) ratios of 63 (C_5HD^+) and 62 ($C_5D^+/C_5H_2^+$).

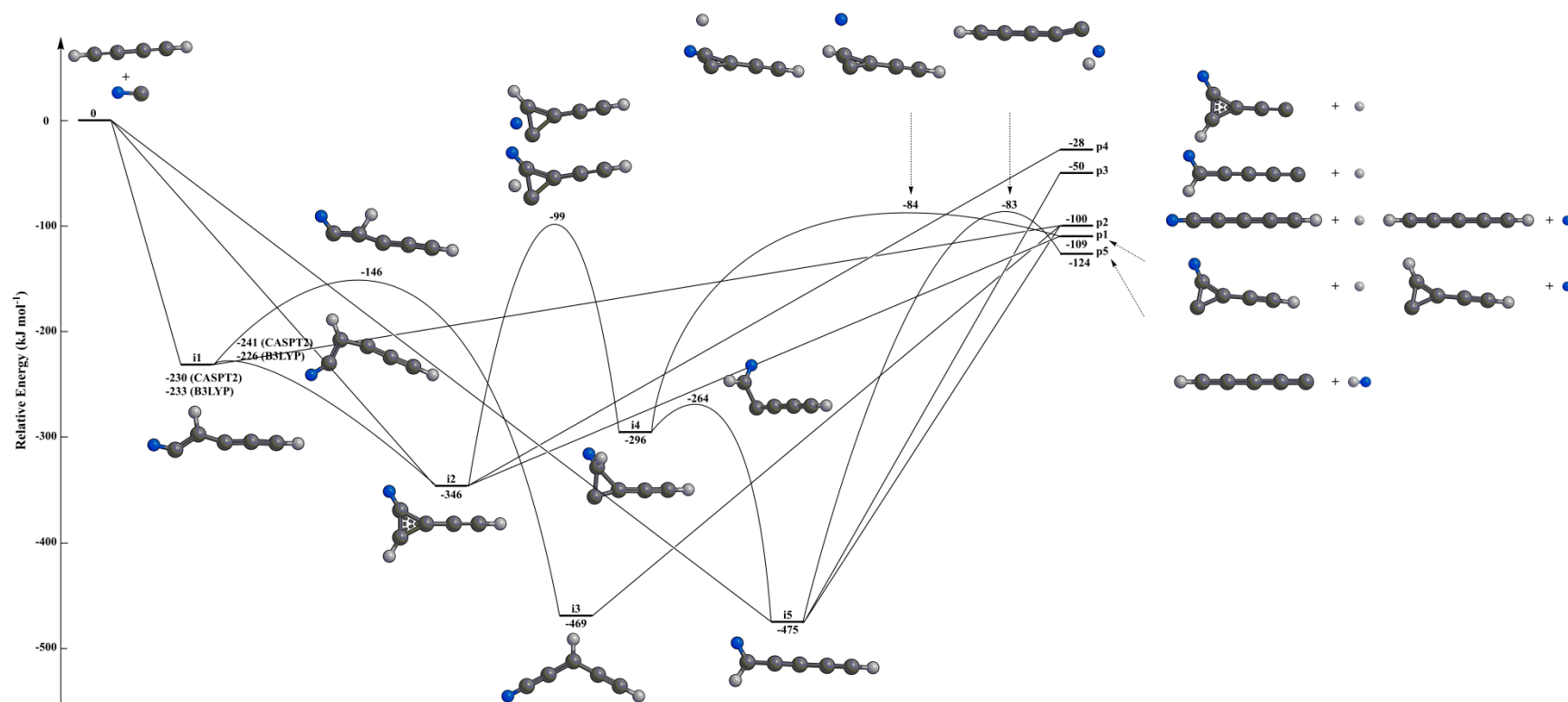


Figure S2. Schematic representation of the potential energy surface of the reaction of the methylidyne-d radical with diacetylene. Energies are given for the fully hydrogenated reactant; energies of the (partially) deuterated species differ by a few kJ mol^{-1} at most. Colors of the atoms: carbon (light black), deuterium (blue) and hydrogen (grey).

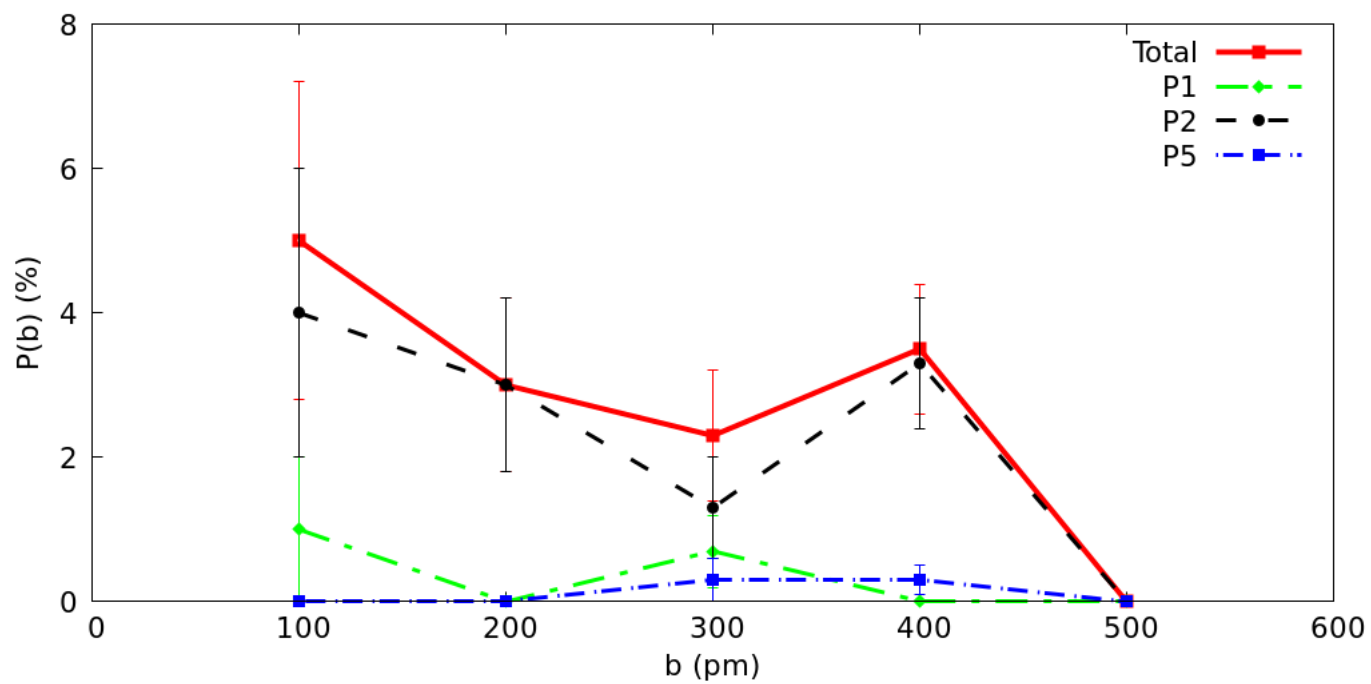


Figure S3. Reaction probability $P(b)$ vs impact parameter b in pm.

Table S1. Peak velocities (v_p) and speed ratios (S) of the diacetylene (HCCCCH), methylidyne (CH), methylidyne- d_1 (CD) beams along with the corresponding collision energies (E_C) and center-of-mass angles (Θ_{CM}) for each reactive scattering experiment.

Beam	v_p (m s ⁻¹)	S	E_C (kJ mol ⁻¹)	Θ_{CM} (degree)
C ₄ H ₂ (X ¹ Σ_g^+)	630 \pm 15	23.2 \pm 0.3		
CH (X ² Π)	1835 \pm 23	12.2 \pm 1.3	19.4 \pm 0.4	53.8 \pm 0.3
CD (X ² Π)	1810 \pm 27	12.2 \pm 0.9	20.1 \pm 0.4	51.8 \pm 0.3

Table S2. Statistical branching ratios (%) for the reaction of the methylidyne (CH) with diacetylene (HCCCCH) at a collision energy of 19.4 kJ mol⁻¹.^a

p1	p2	p3	p4	p5
20.04	79.1901	0.0749	0.2019	0.4931

^aHere, **p1-p5** denote ethynylcyclopropenylidene, pentadiynylidene, pentatetraenylidene, 2-cyclopropen-1-ylideneethenylidene, and 2,4-pentadiynylidyne.

Table S3. The comparison between each candidate quantum mechanics method with respect to the benchmark value (CCSD(T)-F12/cc-pVQZ-f12//B2PLYPD3/cc-pVTZ). The energy (kJ mol⁻¹) is relative to the separated reactant and with ZPE. N/A: not identified with the method.

Method	MP2	B2PLYP	B3LYP	B97	B98	M05	M06	PBE0	MP2	B2PLYP	B3LYP	B97	B98	M05	M06	PBE0	REF
Basis Set	6-31+G*								6-311++G**								REF
i1	-113	-167	-195	-206	N/A	-257	-236	-274	N/A	-155	-204	N/A	N/A	N/A	-485	N/A	
i2	-286	-327	-361	N/A	-368	-421	-396	N/A	N/A	-315	-351	-364	-358	-409	-387	-406	-346
i3	-403	-455	-479	-487	-487	-498	-489	-512	-398	-449	-474	-483	-483	-492	-484	-507	-469
i4	-244	-264	-306	-321	-317	-358	-333	-351	-241	-250	-292	-309	-305	-344	-320	-339	-296
i5	-383	-470	-502	-510	-509	-520	-510	-534	-380	-464	-497	-506	-505	-513	-506	-529	-475
ts1(i1 i3)	7	-106	-169	-181	N/A	-200	-182	-202	N/A	-85	-167	-183	-176	-189	N/A	-197	-142
ts2(i2 i4)	-43	-68	-108	-124	-118	-184	-155	-163	-50	-63	-101	-120	-113	-209	-147	-160	-99
ts3(i4 p1)	-161	-73	-97	-103	-98	-140	-132	-142	-133	-58	-83	-91	-85	-129	-117	-130	-85
ts4(i4 i5)	N/A	-241	-283	N/A	-293	-303	-292	N/A	N/A	-231	-274	-287	N/A	-293	N/A	N/A	-264
P1+H	-161	-102	-110	-127	-121	-168	-158	-158	-133	-88	-97	-117	-110	-161	-145	-147	-109
P2+H	-35	-139	-139	-149	-148	-168	-153	-178	N/A	-136	-139	-151	-149	-170	-153	-177	-100
P3+H	N/A	-45	-84	-100	-97	-81	-88	-102	N/A	-31	-71	-88	-85	-70	-74	-91	-50
P4+H	-72	-29	-47	-65	-59	-95	-84	-93	-44	-12	-30	-51	-44	-82	-65	-78	-28
RMSD	N/A	25	21	N/A	N/A	57	42	N/A	N/A	35	16	N/A	N/A	N/A	N/A	N/A	0

Method	MP2	B2PLYP	B3LYP	B97	B98	M05	M06	PBE0	MP2	B2PLYP	B3LYP	B97	B98	M05	M06	PBE0	REF
Basis Set	aug-cc-pVDZ								cc-pVDZ								REF
i1	-101	-162	-236	-243	-244	-266	-478	-278	-108	-164	-215	N/A	-218	-257	-486	N/A	
i2	N/A	-318	-351	-364	N/A	-410	-383	-406	N/A	-324	-360	-372	-366	-421	-394	-413	-346
i3	-382	-446	-471	-480	-479	-487	-477	-503	-390	-452	-478	-486	-486	-498	-486	-510	-469
i4	-229	-253	-294	-311	-306	-349	-321	-341	-235	-261	-303	-318	-313	-357	-329	-348	-296
i5	-365	N/A	-494	N/A	-501	-511	-499	N/A	-374	-469	-503	-510	-509	-520	-508	-533	-475
ts1(i1 i3)	2	-93	-175	-188	-181	N/A	N/A	-206	-2	-102	-177	-189	-184	-201	-186	-205	-142
ts2(i2 i4)	-49	-72	-111	-128	-121	-190	-157	N/A	-50	-77	-117	-133	-127	-196	-163	-172	-99
ts3(i4 p1)	-48	-66	-90	-98	-92	-134	-121	-135	-47	-70	-95	-102	-96	-139	-127	-138	-85
ts4(i4 i5)	N/A	N/A	-276	-288	N/A	N/A	-281	-307	-234	-237	-280	-291	N/A	-300	-287	-311	-264
P1+H	-128	-94	-103	-122	-116	-164	-146	-151	-133	-98	-109	-126	-120	-169	-153	-155	-109
P2+H	3	-135	-137	-148	-146	-166	-146	-175	-10	-144	-146	-156	-154	-173	-156	-182	-100
P3+H	107	N/A	N/A	N/A	N/A	N/A	N/A	N/A	-58	-43	-85	-101	-98	-83	-85	-101	-50
P4+H	-42	-20	-38	-58	-52	-89	-71	-84	-47	-25	-45	-64	-58	-97	-79	-90	-28
RMSD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	27	23	N/A	N/A	59	86	N/A	0

Movies: Representative movies for reaction pathways:

S1: $i1 \rightarrow i2 \rightarrow p1 + H$ (H from C_4H_2)

S2: $i1 \rightarrow i2 \rightarrow i1 \rightarrow i5 \rightarrow p2 + H$ (H from C_4H_2)

S3: $i1 \rightarrow i2 \rightarrow i1 \rightarrow p2 + H$ (H from C_4H_2)

S4: $i1 \rightarrow p2 + H$ (H from C_4H_2)

S5: $i2 \rightarrow i1 \rightarrow i5 \rightarrow p2 + H$ (H from CH)

S6: $i5 \rightarrow p2 + H$ (H from C_4H_2)

S7: $i5 \rightarrow p2 + H$ (H from CH)

S8: $i5 \rightarrow p5 + H_2$ pathway

Dataset S1. Optimized Cartesian coordinates and vibrational frequencies for all intermediates, transition states, reactants and products involved in the reactions of the methylidyne radical (CH) with diacetylene (C_4H_2).