

## Supporting Information for

### *Effect of stereoisomeric structure and bond location on the ignition and reaction pathways of hexenes*

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by

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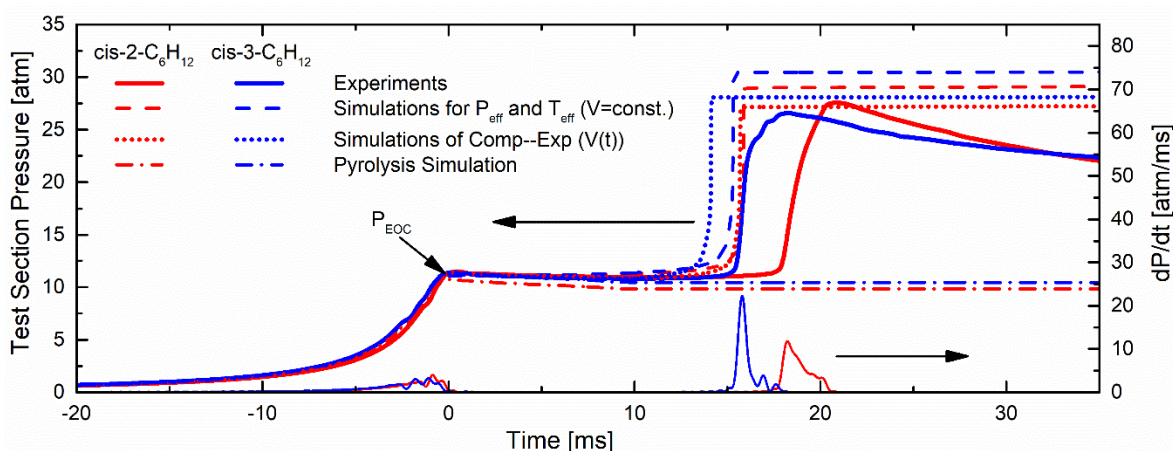
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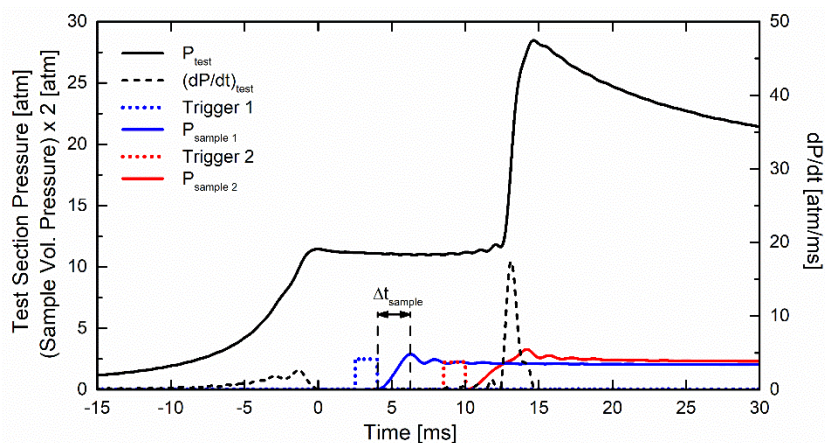
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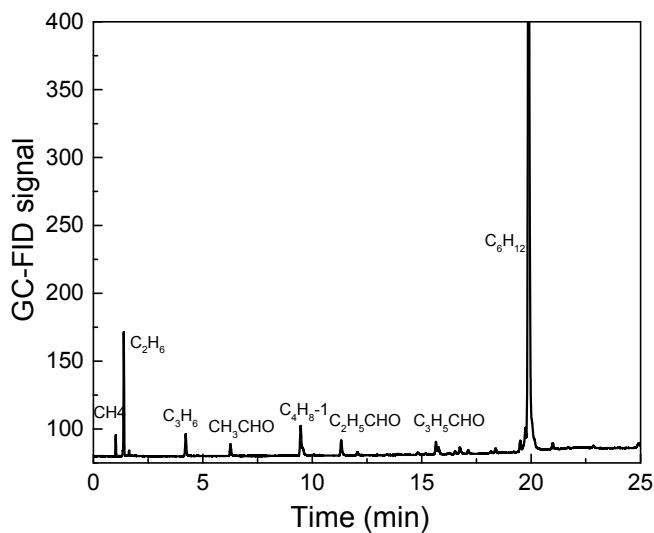


**Figure S1.** Comparison of measured (solid lines) and simulated pressure traces at  $\phi = 0.99$ ,  $P_{\text{eff}} = 11.1$  atm and  $\text{inert}/\text{O}_2 = 7.5$  for cis-2-hexene (red) at  $T_{\text{eff}} = 894$  K, and cis-3-hexene (blue) at  $T_{\text{eff}} = 892$  K. Constant-volume (dashed lines), compression/heat transfer (dotted lines) and pyrolysis (dash-dotted lines) simulations are included for comparison.



**Figure S2.** Typical pressure and pressure-derivative time histories in the test section and the sampling volumes for a cis-2-hexene speciation experiment at  $\phi = 1.0$ ,  $\text{inert}/\text{O}_2 = 7.5$ ,  $P = 11.3$  atm and  $T = 911$  K

with  $\tau_{\text{ign}} = 13.1$  ms. The sampling duration for the first sample is noted in the figure. Two gas samples were acquired during most sampling experiments.



**Figure S3.** Typical gas chromatogram corresponding to the first gas sample from the experimental results presented in **Fig. S2** for cis-2-hexene. The sample was obtained at a normalized sampling time of  $t/\tau_{\text{ign}} = 0.79$ .

**Table S1.** Summary of experimental conditions and results for cis-2-hexene autoignition. All mixture data are provided on a mole fraction basis. Entries with an asterisk (\*) correspond to speciation experiments.

$\phi$	Test Gas Composition				Inert/O <sub>2</sub>	P <sub>eff</sub> [atm]	T <sub>eff</sub> [K]	$\tau_{\text{ign}}$ [ms]
	cis-2-C <sub>6</sub> H <sub>12</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar				
	[%]	[%]	[%]	[%]				
0.99	1.28	11.62	86.94	0.00	7.49	10.5	940	10.0
0.99	1.28	11.62	86.94	0.00	7.49	10.5	941	10.8
0.99	1.28	11.62	78.09	0.00	7.49	10.4	887	21.8
0.99	1.28	11.65	78.09	0.01	7.47	10.6	891	22.6
0.99	1.28	11.63	74.88	12.21	7.49	10.1	980	5.6
0.99	1.28	11.64	74.88	12.21	7.48	10.3	980	5.2
0.99	1.28	11.62	67.50	0.00	7.49	10.4	834	51.8
0.99	1.28	11.62	67.50	0.00	7.49	9.2	809	95.1
0.99	1.28	11.62	82.48	0.00	7.49	11.2	896	18.3
0.99	1.28	11.62	82.48	0.00	7.50	11.1	894	18.2
0.99	1.28	11.62	82.48	0.00	7.49	11.3	897	17.5
0.99	1.28	11.62	82.47	0.00	7.49	10.8	889	21.8
0.99	1.28	11.62	82.47	0.00	7.49	10.5	881	23.0
0.98	1.27	11.66	78.13	0.00	7.47	10.6	899	19.8
0.99	1.28	11.66	74.58	12.26	7.47	10.5	988	4.8
1.00	1.29	11.63	81.70	5.38	7.49	11.6	968	5.6
0.98	1.27	11.67	66.97	0.00	7.46	9.0	803	117.6
0.99	1.28	11.62	74.64	0.00	7.50	9.5	837	52.8
1.00	1.29	11.64	83.54	0.00	7.48	10.4	893	20.4
1.00	1.29	11.63	85.39	0.00	7.49	10.8	904	15.8
1.00	1.29	11.63	85.38	0.00	7.49	10.4	896	18.4
1.00	1.29	11.63	86.70	0.00	7.49	11.0	906	14.5
1.00	1.29	11.63	86.70	0.00	7.49	9.7	881	26.0
1.00	1.29	11.63	86.70	0.00	7.49	10.4	893	20.4
1.00	1.29	11.63	86.74	0.33	7.49	11.3	911	13.1*
1.00	1.29	11.63	86.74	0.33	7.49	11.5	917	11.9*
1.00	1.29	11.64	86.74	0.33	7.48	10.9	913	13.1*
0.99	1.29	11.64	86.74	0.00	7.48	11.1	911	14.0*
0.99	1.29	11.64	86.74	0.00	7.48	10.8	905	16.0*
0.99	1.29	11.64	86.74	0.00	7.48	11.6	918	11.8*
0.99	1.29	11.6401	86.7381	0.00	7.48	11.0	915	12.6*

**Table S2** Summary of experimental conditions and results for cis-3-hexene autoignition. All mixture data are provided on a mole fraction basis. Values with an asterisk (\*) correspond to speciation experiments.

$\phi$	Test Gas Composition				Inert/O <sub>2</sub>	P <sub>eff</sub> [atm]	T <sub>eff</sub> [K]	$\tau_{\text{ign}}$ [ms]
	cis-3-C <sub>6</sub> H <sub>12</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar				
	[%]	[%]	[%]	[%]				
0.99	1.28	11.62	64.08	23.02	7.50	10.9	981	5.0
0.99	1.28	11.62	64.09	23.01	7.49	13.4	1035	2.0
0.99	1.28	11.61	64.08	23.03	7.50	13.6	1042	1.9
0.99	1.28	11.63	64.09	23.00	7.49	13.3	1044	2.2
0.99	1.28	11.66	74.85	12.21	7.47	10.8	989	5.4
0.99	1.28	11.61	86.96	0.00	7.50	10.4	936	9.4
1.00	1.28	11.61	86.95	0.00	7.50	9.8	920	13.3
0.99	1.28	11.63	86.94	0.00	7.49	9.8	918	11.8
0.99	1.28	11.62	86.95	0.00	7.49	10.4	924	11.7
0.99	1.28	11.62	78.10	0.00	7.49	10.2	876	26.6
0.99	1.28	11.62	78.10	0.00	7.50	10.9	884	22.5
0.99	1.28	11.64	68.77	0.01	7.48	10.0	821	76.3
0.99	1.28	11.63	68.76	0.00	7.49	10.8	835	61.1
0.99	1.28	11.65	82.46	0.01	7.47	11.9	908	14.8
0.99	1.28	11.65	85.58	1.47	7.50	11.1	938	8.8
0.99	1.28	11.64	76.69	0.00	7.50	10.1	855	35.8
0.99	1.28	11.65	61.69	25.36	7.50	11.7	1052	1.9
0.99	1.28	11.64	70.43	16.63	7.50	10.8	990	4.8
0.98	1.28	11.74	79.64	0.00	7.50	10.4	879	24.0
0.99	1.28	11.64	86.43	0.64	7.50	12.7	942	7.7
0.99	1.28	11.64	81.87	0.00	7.50	10.8	905	15.1*
0.99	1.28	11.64	81.87	0.00	7.50	10.8	902	17.0*
0.99	1.28	11.64	81.87	0.00	7.50	10.8	905	16.2*
0.99	1.28	11.64	81.87	0.00	7.50	11.0	907	14.9*
0.99	1.28	11.64	81.87	0.00	7.50	10.8	902	17.2*
0.99	1.28	11.65	81.87	0.00	7.50	10.8	903	16.1*
0.99	1.28	11.64	81.87	0.00	7.50	11.0	906	13.9*
0.99	1.28	11.64	81.87	0.00	7.50	10.8	904	15.1*
0.99	1.28	11.64	81.87	0.000	7.50	10.7	902	15.5*

**Table S3.** Summary of results for speciation experiments of cis-2-hexene and cis-3-hexene with an asterisk (\*) in **Tables S1** and **S2**. Data are arranged in ascending order of  $t/\tau_{\text{ign}}$  for each fuel.

Fuel	time [ms]	$\tau_{\text{ign}}$ [ms]	$t/\tau_{\text{ign}}$	cis-C <sub>6</sub> H <sub>12</sub> [ppm]	C <sub>2</sub> H <sub>3</sub> CHO [ppm]	C <sub>3</sub> H <sub>6</sub> [ppm]	CH <sub>3</sub> CHO [ppm]	C <sub>5</sub> H <sub>10</sub> -1 [ppm]	C <sub>4</sub> H <sub>6</sub> -1,3 [ppm]	CO [ppm]	CH <sub>4</sub> [ppm]	CH <sub>3</sub> OH [ppm]	C <sub>2</sub> H <sub>4</sub> [ppm]	C <sub>2</sub> H <sub>6</sub> [ppm]	C <sub>2</sub> H <sub>2</sub> [ppm]	i-C <sub>3</sub> H <sub>5</sub> CHO [ppm]
cis-2-C <sub>6</sub> H <sub>12</sub>	1.82	13.07	0.14	11,090	--	--	53	1	78	--	42	--	112	2	3	10
	2.47	11.94	0.21	11,120	--	--	56	2	88	--	55	--	161	4	3	13
	4.42	13.12	0.34	10,471	1	56	114	2	80	--	70	--	228	5	6	29
	6.04	14.00	0.43	10,295	17	83	181	6	186	--	100	--	297	6	--	39
	7.05	16.02	0.44	9,284	15	80	170	7	147	--	95	10	320	6	7	34
	8.09	13.07	0.62	9,456	20	211	272	15	286	--	180	--	621	20	4	70
	7.44	11.82	0.63	8,849	22	123	304	14	345	--	164	--	575	11	11	69
	8.6	11.94	0.72	7,382	27	173	261	13	339	--	204	--	677	23	--	66
	10.35	13.12	0.79	6,835	58	374	578	17	558	1,988	520	--	1,590	67	--	126
	12.25	14.00	0.88	3,158	24	--	156	--	229	364	141	--	404	16	13	--
	11.07	12.56	0.88	6,447	27	362	551	26	469	1,746	602	--	1,766	76	21	119
12.81	12.56	1.02	1,668	4	57	73	8	100	4,599	199	71	503	35	--	19	
cis-3-C <sub>6</sub> H <sub>12</sub>	3.45	16.97	0.20	10,690	37	10	11	3	--	--	37	--	95	2	--	35
	5.47	16.18	0.34	10,583	62	22	23	4	--	--	58	6	164	4	3	47
	7.17	15.48	0.46	9,550	112	43	41	8	--	--	97	45	298	10	--	77
	7.46	14.85	0.50	9,871	109	36	43	8	--	--	119	--	339	10	3	86
	10.21	16.14	0.63	9,185	155	61	67	11	--	--	147	--	461	13	5	107
	10.83	15.10	0.72	8,739	189	63	108	15	10	--	228	--	654	21	10	134
	13.20	16.97	0.78	4,684	100	32	66	11	--	--	119	13	341	12	40	75
	13.28	15.48	0.86	3,530	87	38	82	9	--	372	141	30	387	19	48	76
	13.02	15.07	0.86	6,617	215	108	203	24	132	1,800	392	108	1,054	49	136	171
	14.04	16.18	0.87	--	--	--	--	--	--	--	--	--	16	--	--	--
	15.57	17.23	0.90	4,317	116	112	188	16	202	3,983	455	--	888	73	119	110
14.69	15.07	0.97	3,062	57	63	74	8	112	3,669	322	29	487	72	133	54	

13.56	13.85	0.98	5,277	138	137	206	20	223	9,827	776	138	1,304	141	291	134
15.19	15.10	1.01	981	19	18	18	3	99	2,153	158	--	205	44	479	22
15.21	14.85	1.02	1,239	29	44	27	7	102	6,148	368	--	371	99	175	28

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