

Supplementary Material for

Phenalenyl growth reactions and implications to prenucleation chemistry of aromatics in flames

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The Supplementary Information contains:

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Table S1: Parameters of fitted modified Arrhenius expressions $k = A T^n \exp(-E_a/RT)$ or $k = A_1 T^{n1} \exp(-E_a^1/RT) + A_2 T^{n2} \exp(-E_a^2/RT)$ for the considered reactions

Table S2: Reaction model for the ODE kinetic test

Additional files:

rateConstants.xlsx: extended set of rate constants

C13H8+C2H2_rate_constants_pccp.xlsx: calculated rate constants for reactions (1), (3), and (4) at various temperatures and pressures

***.inp:** input files for RRKM-ME calculations of rate constants for reactions (2) and (4) and TST calculations for reactions (1) and (3) using MESS

***.dat:** input files containing intersystem crossing reaction fluxes requires for RRKM-ME/NST calculations of rate constants for reaction (4)

Table S1. Parameters of fitted modified Arrhenius expressions $k = A T^n \exp(-E_a/RT)$ or $k = A_1 T^{n1} \exp(-E_a^1/RT) + A_2 T^{n2} \exp(-E_a^2/RT)$ for the considered reactions. Pre-exponential factors A are in $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ for bimolecular reactions and in s^{-1} for unimolecular reactions, E_a are in cal mol^{-1} .

Reaction	p , atm	A	n	E_a	T range, K
$\pi\text{A2A}\bullet + \text{C}_2\text{H}_2 \rightarrow \text{i4}''\text{t}$	PLOG/3.000E-02	8.98E+140	-40.191	50787	500-1000
	PLOG/3.000E-02	1.54E+110	-31.747	31379	
	PLOG/1.000E+00	7.04E+134	-36.615	62202	500-1250
	PLOG/1.000E+00	3.71E+87	-23.368	31362	
	PLOG/1.000E+01	-9.83E+106	-28.195	47380	500-1500
	PLOG/1.000E+01	1.64E+84	-21.189	38041	
	PLOG/1.000E+02	7.83E+10	1.1615	12293	500-1750

	PLOG/1.000E+02	-1.98E+27	-3.1659	31488	
$\pi A2A\bullet + C_2H_2 \rightarrow i4''s$	PLOG/3.000E-02	1.53E+78	-21.02	25188	500-1500
	PLOG/3.000E-02	1.69E+149	-40.94	73251	
	PLOG/1.000E+00	-4.51E+51	-11.276	36469	500-1800
	PLOG/1.000E+00	6.58E+20	-2.9498	5647.4	
	PLOG/1.000E+01	1.91E+42	-9.8188	13447	500-2000
	PLOG/1.000E+01	6.90E+105	-27.236	62255	
	PLOG/1.000E+02	7.49E+15	-2.365	-1168.4	500-2250
	PLOG/1.000E+02	3.15E+89	-22.202	60056	
$\pi A2A\bullet + C_2H_2 \rightarrow p1'' + H$	PLOG/3.000E-02	1.94E+31	-4.5856	33803	500-2500
	PLOG/3.000E-02	4.13E+10	0.7653	13968	
	PLOG/1.000E+00	1.53E+33	-5.1045	35696	500-2500
	PLOG/1.000E+00	5.68E+13	-4.42E-02	16812	
	PLOG/1.000E+01	3.08E+31	-4.6266	34137	500-2500
	PLOG/1.000E+01	1.72E+16	-0.83778	19155	
	PLOG/1.000E+02	1.10E+43	-7.7334	46061	500-2500
	PLOG/1.000E+02	3.61E+09	1.2006	18284	
$p1'' + H \rightarrow \pi A2A\bullet + C_2H_2$	PLOG/3.000E-02	2.32E+37	-6.0228	44657	500-2500
	PLOG/3.000E-02	8.82E+16	-0.73841	25062	
	PLOG/1.000E+00	5.60E+38	-6.3993	46121	500-2500
	PLOG/1.000E+00	2.18E+20	-1.6305	27982	
	PLOG/1.000E+01	3.33E+37	-6.0516	44958	500-2500
	PLOG/1.000E+01	3.22E+22	-2.3266	30219	
	PLOG/1.000E+02	1.33E+49	-9.1721	56924	500-2500
	PLOG/1.000E+02	7.07E+15	-0.29153	29366	
$\pi A2A\bullet + C_2H_2 \rightarrow \pi A2AR5(p2'') + H$	PLOG/3.000E-02	4.71E+41	-7.8405	28851	500-2500
	PLOG/3.000E-02	1.12E+40	-8.038	17831	
	PLOG/1.000E+00	5.85E+42	-8.2379	27041	500-2500
	PLOG/1.000E+00	1.64E+00	3.5213	2481.4	
	PLOG/1.000E+01	2.96E+55	-11.596	41074	500-2500
	PLOG/1.000E+01	1.12E+132	-37.264	55175	
	PLOG/1.000E+02	-3.87E+68	-15.706	47637	500-2500
	PLOG/1.000E+02	4.28E+44	-8.4531	36844	
$\pi A2AR5(p2'') + H \rightarrow \pi A2A\bullet + C_2H_2$	PLOG/3.000E-02	2.53E+49	-9.143	68832	500-2500
	PLOG/3.000E-02	2.15E+47	-9.2034	57739	
	PLOG/1.000E+00	5.82E+50	-9.6103	67337	500-2500
	PLOG/1.000E+00	1.83E+07	2.4095	42132	
	PLOG/1.000E+01	3.32E+63	-12.983	81407	500-2500
	PLOG/1.000E+01	4.15E+139	-38.517	95196	
	PLOG/1.000E+02	9.03E+71	-15.063	96022	500-2500
$p1'' + H \rightarrow i4''t$	PLOG/3.000E-02	2.32E+111	-30.931	40300	500-1000
	PLOG/1.000E+00	2.99E+137	-37.103	67482	500-1250
	PLOG/1.000E+00	2.55E+87	-23.025	35030	
	PLOG/1.000E+01	-1.17E+108	-28.318	51327	500-1500
	PLOG/1.000E+01	2.94E+84	-21.066	41591	
	PLOG/1.000E+02	3.69E+14	0.20528	17117	500-1750

	PLOG/1.000E+02	-4.33E+23	-2.0876	30473	
p1'' + H → i4''s	PLOG/3.000E-02	-1.94E+125	-34.591	50283	500-1500
	PLOG/3.000E-02	8.01E+97	-26.217	38663	
	PLOG/1.000E+00	5.80E+116	-30.636	65592	500-1800
	PLOG/1.000E+00	1.48E+63	-15.935	23928	
	PLOG/1.000E+01	6.47E+32	-6.1685	17532	500-2000
	PLOG/1.000E+01	-2.06E+82	-19.394	71231	
	PLOG/1.000E+02	1.69E+20	-3.261	5705.9	500-2250
	PLOG/1.000E+02	7.03E+130	-33.46	98207	
p1'' + H → πA2AR5 (p2'') + H	PLOG/3.000E-02	8.04E+48	-10.467	25456	500-2500
	PLOG/3.000E-02	3.83E+48	-9.6929	36415	
	PLOG/1.000E+00	1.21E+54	-11.381	36790	500-2500
	PLOG/1.000E+00	2.61E+20	-1.9748	17098	
	PLOG/1.000E+01	8.72E+62	-13.604	49005	500-2500
	PLOG/1.000E+01	3.77E+117	-32.367	55178	
	PLOG/1.000E+02	2.43E+80	-18.142	72080	500-2500
	PLOG/1.000E+02	2.83E+31	-5.0241	31348	
πA2AR5 (p2'') + H → p1'' + H	PLOG/3.000E-02	7.57E+50	-9.7305	66299	500-2500
	PLOG/3.000E-02	5.32E+48	-9.7753	53853	
	PLOG/1.000E+00	2.71E+54	-10.862	65246	500-2500
	PLOG/1.000E+00	5.83E+17	-0.66171	43716	
	PLOG/1.000E+01	7.76E+64	-13.549	78449	500-2500
	PLOG/1.000E+01	4.19E+113	-30.469	82386	
	PLOG/1.000E+02	-4.30E+43	-6.5241	91431	500-2500
	PLOG/1.000E+02	8.26E+19	-0.38406	58632	
πA2AR5 (p2'') + H → i4''t	PLOG/3.000E-02	3.05E+108	-28.59	48739	500-1000
	PLOG/3.000E-02	4.59E+60	-15.00	19851	
	PLOG/1.000E+00	9.37E+94	-23.858	49882	500-1250
	PLOG/1.000E+00	5.98E+41	-8.83	14722	
	PLOG/1.000E+01	5.28E+82	-19.876	48343	500-1500
	PLOG/1.000E+01	4.21E+32	-5.8908	11942	
	PLOG/1.000E+02	2.41E+59	-12.867	38160	500-1750
	PLOG/1.000E+02	2.41E+26	-3.9196	9837.8	
i4''t → πA2AR5 (p2'') + H	PLOG/3.000E-02	2.67E+03	3.342	32224	500-1000
	PLOG/3.000E-02	-1.82E+65	-14.477	70948	
	PLOG/1.000E+00	5.37E+85	-21.109	75007	500-1250
	PLOG/1.000E+00	5.07E+40	-8.4483	44713	
	PLOG/1.000E+01	2.40E+70	-16.293	70774	500-1500
	PLOG/1.000E+01	1.47E+31	-5.3955	41746	
	PLOG/1.000E+02	1.11E+55	-11.624	65255	500-1750
	PLOG/1.000E+02	2.63E+24	-3.2514	39554	
πA2AR5 (p2'') + H → i4''s	PLOG/3.000E-02	1.02E+119	-30.227	63674	500-1500
	PLOG/3.000E-02	8.76E+42	-8.8313	10519	
	PLOG/1.000E+00	9.30E+14	-8.62E-02	556.84	500-1800
	PLOG/1.000E+00	-1.09E+102	-23.442	92302	
	PLOG/1.000E+01	5.88E+84	-19.67	54355	500-2000

i4''s πA2AR5 (p2'') + H	→	PLOG/1.000E+01	1.42E+31	-5.0105	7627.6	500-2250
		PLOG/1.000E+02	1.74E+50	-9.9044	29433	
		PLOG/1.000E+02	1.80E+25	-3.3143	4790.1	
		PLOG/3.000E-02	4.16E+116	-29.212	128490	500-1500
		PLOG/3.000E-02	8.49E+43	-8.7812	77673	
		PLOG/1.000E+00	5.33E+15	4.48E-02	6.77E+04	500-1800
		PLOG/1.000E+00	-5.62E+96	-21.715	152400	
		PLOG/1.000E+01	2.13E+82	-18.701	1.18E+05	500-2000
		PLOG/1.000E+01	3.90E+32	-5.0971	74976	
A2AH + H → πA2A + H ₂		PLOG/1.000E+02	4.66E+50	-9.7335	95267	500-2250
		PLOG/1.000E+02	2.70E+27	-3.6426	72321	
A2AH + H → πA2A + H ₂		independent of <i>p</i>	8.54E+08	1.6186	2014.6	500-2500
πA2A + H ₂ → A2AH + H		independent of <i>p</i>	3.58E+06	2.3411	41821	500-2500
πA2A + H → πA2A• + H ₂		independent of <i>p</i>	2.22E+08	1.9004	14295	500-2500
πA2A• + H ₂ → πA2A + H		independent of <i>p</i>	10783	2.6538	4727.9	500-2500

Table S2. Reaction model for the ODE kinetic test (unit of *k*'s are mol/cm³, s; extended set of *k*'s is in the rateConstants.xlsx file).

rxn No	reaction	k_Forw (1500 K)	k_Rev (1500 K)	source
1	A2 + H <=> A2-1 + H2	1.80E+12	8.98E+11	1
2	A2-1 + H <=> A2	1.26E+14	0	2
3	A2-1 + C2H2 <=> A2R5 + H	1.33E+12	6.52E+09	3
4	A2 + H <=> A2-2 + H2	1.72E+12	8.06E+11	1
5	A2-2 + H <=> A2	1.13E+14	0	2
6	A2-1 <=> A2-2	1.32E+05	1.21E+05	4
7	A2-1 + C2H2 <=> A2C2H + H	1.24E+11	2.77E+11	3
8	A2C2H + H <=> A2C2H* + H2	3.19E+11	4.33E+11	1
9	A2C2H* + H <=> A2C2H	1.13E+14	0	2
10	A2C2H* + C2H2 <=> A3-1	3.51E+11	5.16E+02	4
11	A2C2H* + C2H2 <=> A3-2	1.96E+11	2.65E+02	4
12	A3 + H <=> A3-1 + H2	3.19E+11	4.33E+11	1
13	A3-1 + H <=> A3	1.13E+14	0	2
14	A3 + H <=> A3-2 + H2	3.19E+11	4.33E+11	1
15	A3-2 + H <=> A3	1.13E+14	0	2
16	A3-1 <=> A3-2	1.32E+05	1.21E+05	4
17	A2R5 + H <=> A2R5* + H2	3.19E+11	4.33E+11	1
18	A2R5* + H <=> A2R5	1.13E+14	0	2
19	A2R5* + C2H2 <=> A2R5C2H + H	3.58E+11	1.27E+12	5
20	A2R5C2H + H <=> A3-2	2.71E+11	4.03E+04	5
21	A3-1 + C2H2 <=> A4 + H	5.33E+11	0	3
22	A2C2H + H <=> A2R5 + H	3.49E+12	0	3
23	A2-2 + C2H2 <=> A2C2H_2 + H	1.82E+12	3.32E+12	3
24	A2C2H_2 + H <=> A2C2H*2 + H2	4.50E+11	8.68E+11	1
25	A2C2H*2 + H <=> A2C2H_2	1.26E+14	0	2
26	A2C2H*2 + C2H2 <=> A3-2	3.51E+11	5.16E+02	4
27	A2R5 + H <=> A2R5- + H2	5.54E+10	6.39E+11	5

28	A2R5- + H <=> A2R5	1.68E+14	0	2
29	A2R5- + CH3 <=> π A2A + H	2.74E+13	0	6
30	π A2A + H <=> π A2A• + H2	2.09E+12	6.29E+11	present work
31	π A2A• + H <=> π A2A	1.26E+14	0	2
32	π A2A• + C2H2 <=> π A2AR5 + H	5.00E+12	2.20E+10	present work
33	A2R5 + H <=> 2-A2R5 + H2	5.54E+10	6.39E+11	5
34	2-A2R5 + H <=> A2R5	1.68E+14	0	2
35	2-A2R5 + C2H2 <=> R5A2R5 + H	1.33E+12	6.52E+09	3
36	R5A2R5 + H <=> R5A2R5- + H2	5.54E+10	6.39E+11	5
37	R5A2R5- + H <=> R5A2R5	1.68E+14	0	2
38	R5A2R5- + CH3 <=> π A2AR5 + H	2.74E+13	0	6
39	π A2AR5 + H <=> π A2AR5- + H2	5.54E+10	6.39E+11	5
40	π A2AR5- + H <=> π A2AR5	1.68E+14	0	2
41	π A2AR5- + CH3 <=> A4 + H	2.74E+13	0	6

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