A chemical kinetic modeling study of indene pyrolysis

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Abstract

An improved polycyclic aromatic hydrocarbon (PAH) model is developed to predict the decomposition of indene and the formation of large PAHs under pyrolytic conditions. This model is developed based on experimental study of pyrolytic kinetics of indene in a flow reactor at low and atmospheric pressures (30 and 760 Torr) by using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). A general map of PAH growth is presented according to the observations in this study and those in literature. Indene dissociates via indanyl forming mono-cyclic aromatics and small intermediates, while its dominant decomposition product is indenyl. As a resonantly stabilized radical, indenyl serves as a platform molecule in PAH growth process which links small unsaturated hydrocarbons and mono-aromatic species to multi-cyclic ones. Reactions of indenyl radical are proposed to form commonly studied and recently observed PAHs. Rate constants of these reactions are evaluated by analyzing literature data of rate constant measurements, quantum chemical calculations and analogy to cyclopentadienyl radical. The main PAH formation pathways are the bimolecular addition reactions of indenyl radical with indene and a series of intermediates, forming C₁₀-C₁₈ and larger PAHs. Meanwhile, radical chain reactions provide huge passage for PAH growth form

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24 one resonantly stabilized radical (RSR) to larger ones. Particular contribution has been found from the
25 reactions of RSRs that have five-member ring in their molecular structures, such as fluorenyl, benz-
26 indenyl, cyclopenta-phenanthrenyl and benzo-fluorenyl.

27 **Keywords:** *Indene mechanism; Flow reactor pyrolysis; SVUV-PIMS; Polycyclic aromatic hydrocarbons;*
28 *Resonantly stabilized radical.*

29

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and soot are formed as a result of incomplete combustion, and contribute to particulate matter (PM) in our atmosphere. Human exposure to high density of PM enhances the chances of heart and lung diseases [1,2]. The investigation of the formation of PAHs and soot has, therefore, gained increasing attention since 1990s [3-6]. Various PAH models have been developed with a large array of possible reactions [7-15]. Herein, we briefly review the reaction kinetics for bicyclic aromatic species in these models.

In a general view of the history of PAH model development, modelers generally aim to fill the blanks in the giant map of PAH species. Wang et al. [16] proposed hydrogen-abstraction-carbon-addition (HACA) mechanism in 1994, which was later supported by a number of experimental and theoretical investigations [13,17-20]. Models developed by Wang et al. [14] and Appel et al. [13] were then reported to describe the formation and growth of PAHs in flames fueled by C₂ hydrocarbons, such as ethane, ethylene and acetylene. These models focused on HACA routes, and had relatively less consideration on toluene, indene, methylnaphthalene, etc., which may have high quantities in flames [15,21-23]. Later, Marinov et al. [12] extended the PAH model to cyclopenta[*cd*]pyrene, a C₁₈ PAH, and Richter et al. [11] described the PAH growth up to coronene. They even proposed reaction pathways to form C₆₀-C₇₀ fullerene. These two works represented early investigations that not only included HACA mechanism but also the contributions from radical combination routes [12,24-29]. Propargyl and cyclopentadienyl radicals were then considered to be efficient contributors to the formation of first and second aromatic ring, respectively [4,15,30-38]. Slavinskaya et al. [10,39] reviewed previous investigations and developed a PAH model up to five aromatic rings. Their model was validated against literature experimental data and provided semi-detailed chemical information for the PAH formation pathways. Later, Shulka and Koshi [40] added phenyl and methyl addition reactions in their model to extended the HACA mechanism. Hansen et al. [41] proposed repetitive addition of methyl and acetylene for PAH growth. A series of radical-involved PAH formation pathways have been proposed and calculated [42-54]. Finally, a number of PAH models [7-9,19,30,55-

56 58] have thus been developed and validated. We will not detail those studies here but will instead
57 discuss some recent works, particularly those closely related on indene.

58 A recent study of Johansson et al. [59] has conformed the critical role of resonantly stabilized
59 radicals (RSR) in the growth of PAH and soot. Some recent theoretical calculations also revealed
60 details of the reaction mechanisms of RSRs combination [47,48]. All these kinetic developments
61 provide a good opportunity to model the PAH growth process from bicyclic aromatics to very large
62 ones. Indene (C_9H_8) is a typical bicyclic aromatic species, which is an important transmitting platform
63 in the aromatic growth sequence. It could produce indenyl (C_9H_7) radical *via* H-abstraction or H-
64 elimination reactions. Indenyl radical has a resonantly stabilized molecular structure, and is, therefore,
65 very participative in radical-radical and radical-neutral recombination reactions [59,60]. Small
66 molecules can form indene or indenyl radical through multiple pathways, and then grow to large PAHs.
67 Kinetic modeling study on indene can help reveal not only indenyl-involved PAH growth pathways
68 but also the aggregation of small molecules formed by the decomposition of indene.

69 There are only a few literature studies related to indene chemical kinetics [61-67]. Badger and
70 Kimber [67] performed gas chromatography (GC) measurements of indene pyrolysis, and observed
71 significant amount of benzofluorenes, benz[a]anthracene, benzo-phenanthrene and chrysene. Laskin
72 and Lifshitz [62] measured thermal decomposition products of indene behind reflected shock waves
73 also by GC. Indenyl and indanyl radicals were recommended in their work as the main pathways of
74 indene consumption. Benzene, toluene and phenylacetylene were proposed to be formed *via* five-
75 member ring dissociation of indanyl radical, while the decomposition of indenyl formed 1-ethynyl-
76 cyclopenta-2,4-dienide (C_7H_5) and cyclopentadienyl (C_5H_5) radicals. Flash pyrolysis of 2-ethynyl-
77 toluene ($C_2HC_6H_4CH_3$) was studied in the work of Ajaz et al. [61], and that of 3-methyl-4-(2'-
78 methyl)benzylideneisoxazol-5(4H)-one by Wentrup et al. [63]. The quantum chemical calculations of
79 Wentrup et al. [63] explained the interconversion between indene and 2-ethynyl-toluene by Roger-
80 Brown rearrangement. Lifshitz et al. [66] investigated the pyrolysis of 2-methyl-indene in a shock tube,
81 and described the mechanism of indenyl radical according to their experimental observations.

82 Literature quantum chemical investigations of indene have focused on the addition reactions of indenyl.
83 The addition of acetylene on indenyl radical was calculated in the work of Cavallotti et al. [64]. In a
84 recent study, Mebel et al. [53] proposed the conversion from indene to naphthalene, emphasizing that
85 1-methyl-indene and 1-methyl-indenyl are critical intermediates in this process. The reaction between
86 indene and indenyl radical was investigated by Lu and Mulholland [65] *via* quantum chemical
87 calculations and species identification experiment. They proposed the product of this 9-step
88 mechanism to be chrysene, similar to the formation of naphthalene from cyclopentadienyl.
89 Calculations of Wentrup et al. [63] also showed that the combination of indenyl could produce bi-
90 indene and chrysene.

91 In the current work, detailed experimental data of indene pyrolysis in a flow reactor are reported
92 and used to propose a new model for indene kinetics. Experiments were performed with synchrotron
93 vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) combined with molecular-beam
94 sampling technique [68,69]. Indene-contributed PAH sub-mechanism is constructed based on the
95 present experimental measurements and quantum chemical calculations. The major improvement in
96 the present model is the inclusion of semi-detailed PAH growth pathways *via* indenyl-involved
97 reactions. The model is validated against experimental data from this study and literature. Important
98 intermediates and reactions are identified for their critical role in the decomposition and ring expansion
99 of indene.

100

101 **2. Experimental details**

102 Indene pyrolysis was studied in a flow reactor at an undulator-based VUV beamline (BL03U) of
103 Hefei Light Source (HLS II), China. This new pyrolysis facility and the experimental evaluation
104 process have been introduced in detail in previous works [68,69]; only a brief description will be given
105 here. The flow reactor is composed of a home-made furnace and an α -type alumina ceramic tube (inner
106 diameter 7.0 mm, wall thickness 1.5 mm). Electrically heated wire is uniformly twined in the inner
107 layer of the furnace, and the outermost layer acts as a heat shield. The total length of the heating zone

108 is ~ 220 mm. A tungsten–rhenium (W–Re) thermocouple is positioned at the middle region to control
109 the reactor temperature. For the experiments reported here, mixtures of argon and indene were fed into
110 the alumina tube in the gas phase, and the pyrolysis species were sampled 10 mm downstream from
111 the outlet of the ceramic tube by a quartz nozzle. The forming molecular beam was passed through a
112 skimmer, and ionized by an orthogonal tunable VUV light. Ions were detected by a time-of-flight mass
113 spectrometer (TOF-MS) *via* an ion introducer.

114 Since temperature along the centerline of the flow reactor is a key parameter for the pyrolysis
115 process in the flow reactor, accurate temperature profiles were measured by an S-type thermocouple
116 before/after each measurement. Details about the temperature measurement are provided in *SMM2*
117 Section 1.1. The measured temperature profiles are given in *SMM1*, which are used in the simulation
118 of the flow reactor [70].

119 Liquid indene (purity 97%) is injected in a vaporizer at 485 K before being fed into the flow
120 reactor. It is regulated by a high-pressure chromatography pump, while argon (purity 99.99%) is
121 regulated by an MKS mass flow controller. The molar composition of the mixture is 0.32% indene /
122 99.68% argon, and the total flow rate of the mixture is 1.5 SLM. Measurements of photoionization
123 efficiency (PIE) and mass spectra were carried out at two pressures, 30 and 760 Torr, and temperature
124 was varied in steps of 25 K over 975 – 1450 K. The residence time is estimated to be 20 and 500 ms
125 at 30 and 760 torr, respectively. The uncertainty of SVUV-PIMS measurements comes primarily from
126 the sampling process and the photoionization cross-sections (PICS) of the measured species [68].
127 Generally, the measurement uncertainty is $\pm 10\%$ for species with direct PICS measurement, $\pm 25\%$ for
128 stable species with PICS available in literature or database, and a factor of 2 for free radicals (usually
129 underestimated due to annihilation in the sampling process) and species with estimated PICS. Further
130 details of the experimental methodology, such as purity of indene, mole fraction evaluation, carbon
131 balance at each temperature, and PICSs of various species, are given in *SMM2*.

132

3. Theoretical calculations

Quantum chemical calculations were employed in this work for the molecular structures, bond energies and reaction pathways. Geometry optimizations, electronic energies, and frequencies were computed using M08-HX method [71] with the MG3S basis set [72]. The MG3S basis set is identical to the 6-311+G(2df,2p) basis set for H, C, and O atoms [73]. Self-consistent field calculations and geometry optimization were performed with tight convergence criteria. Density functional integrations were carried out by a grid of 99 radial shells per atom with 974 angular points per shell. All calculations were performed using the Gaussian 16 software [74] with a self-developed MN-GFM6.7 module [75]. M08-HX/MG3S method was selected as an affordable electronic structure method because it has been shown to have uncertainty below 1 kcal/mol [76]. Cartesian coordinates (in Å) and absolute energies of M08-HX/MG3S optimized geometries are collected in *SMM3*.

4. Improved kinetic model

We roughly divided indene model into two parts: the decomposition routes and the aromatic growth routes. The first part of the current model is referred to the base models from Yuan et al. [9,56], Pousse et al. [77] and Lifshitz et al. [66]. The second part of the model is the PAH growth from indenyl radical. The model of Yuan et al. is adopted as the base model, and then we built up reaction blocks for large PAHs. We intended to keep the rate constants in the base model, and added necessary PAH formation reactions driven by indenyl. Rate constants of these reactions are taken either from values in the literature [40,47,50,62,65,66,78] or analogized to similar reactions of cyclopentadienyl radical [46,48,51,64,79].

Table 1 Selected reactions in the present model

No.	Reactions	$A^\#$	n	$E_a^\#$	Ref.
1	$C_9H_7 + H (+M) = C_9H_8 (+M)$	1.10×10^{14}	0	0	a
	low	4.40×10^{80}	-18.28	12994	
	troe	0.068	400.7	4135.8	5501.9
	$H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/$				

2	$C_9H_8 + H = C_9H_7 + H_2$		2.22×10^{15}	1.874	4259	b
3	$C_9H_8 + H = C_9H_9^1$		6.50×10^{12}	0	3100	[79]
4	$C_9H_8 + H = C_9H_9^2$		5.50×10^{12}	0	7000	[79]
5	$C_9H_7 + CH_3 = C_9H_7^1CH_3$		8.34×10^{15}	-0.7	-500	[51]
6	$C_9H_6^3CH_3 = C_9H_7^1CH_2$		2.42×10^{28}	1	52470	[78]
7	$C_9H_7^1CH_2 = C_{10}H_9^1$		2.42×10^{28}	1	12282	[78]
8	$C_9H_7^2CH_2 = C_{10}H_9^2$		2.42×10^{28}	1	50520	[78]
9	$C_{10}H_9^2 = C_{10}H_9^1$		2.42×10^{28}	1	6970	[78]
10	$C_{10}H_9^1 = bC_{10}H_9$		2.42×10^{28}	1	15120	[78]
11	$C_9H_7^2CH_2 = C_{10}H_9^3$		2.42×10^{28}	1	53950	[78]
12	$C_{10}H_9^3 = C_{10}H_9^4$		2.42×10^{28}	1	21090	[78]
13	$C_{10}H_9^4 = aC_{10}H_9$		2.42×10^{28}	1	42270	[78]
14	$aC_{10}H_9 = C_{10}H_8 + H$		2.42×10^{28}	-5.83	23947	[80]
15	$bC_{10}H_9 = C_{10}H_8 + H$		2.42×10^{28}	-5.83	23947	[80]
16	$C_9H_7 + CH_3 = C_9H_6^3CH_3 + H$					c
	plog	0.01	8.13×10^{25}	-3.51	41018	
	plog	1	3.83×10^{26}	-3.69	41579	
	plog	10	1.16×10^{33}	-5.47	47110	
	plog	100	1.03×10^{48}	-9.54	61181	
17	$C_9H_7^1CH_3 + H = C_9H_8 + CH_3$		8.00×10^{13}	0	10000	[66]
18	$C_9H_7^2CH_3 + H = C_9H_8 + CH_3$		8.00×10^{13}	0	10000	[66]
19	$C_9H_7^3CH_3 + H = C_9H_8 + CH_3$		8.00×10^{13}	0	10000	[66]
20	$C_9H_7 + C_2H_2 = C_9H_7C_2H + H$					d
	plog	0.0001	5.58×10^{11}	-0.1	34720	
	plog	0.001	4.55×10^7	1.52	24370	
	plog	0.01	5.75×10^6	1.79	24100	
	plog	0.1	4.52×10^7	1.54	24710	
	plog	1	8.17×10^{11}	0.33	27430	
	plog	10	4.40×10^{15}	-0.68	30890	
	plog	100	7.24×10^{15}	-0.61	34040	
	plog	1000	1.88×10^7	2.07	34340	
21	$A_2^1CH_2 \Rightarrow C_9H_7C_2H + H$					e
	plog	0.013	4.47×10^{129}	-32.57	162410	
	plog	0.130	1.29×10^{123}	-30.34	163830	
	plog	1.000	2.95×10^{97}	-22.95	148280	
	plog	1.500	8.20×10^{14}	0	80700	
	plog	10.00	1.26×10^{39}	-6.76	99710	
	plog	50.00	1.44×10^{13}	0.453	76300	
22	$C_9H_7C_2H + H \Rightarrow A_2^1CH_2$		8.80×10^8	1.2	-2020	f
23	$A_2^1CH_2 = cC_{11}H_9$					g
	plog	0.013	1.12×10^{128}	-32.57	162410	
	plog	0.130	3.23×10^{121}	-30.34	163830	
	plog	1.000	7.38×10^{95}	-22.95	148280	
	plog	1.500	2.05×10^{13}	0	80700	
	plog	10.00	3.15×10^{37}	-6.76	99710	
	plog	50.00	3.60×10^{11}	0.453	76300	
24	$cC_{11}H_9 + H = A_2^1CH_2 + H$		2.20×10^{63}	-13	58628	h
25	$cC_{11}H_9 + H = A_2^- + CH_3$		1.20×10^{61}	-12.4	57003	i
26	$C_9H_7 + C_2H_2 = cC_{11}H_9$					j

	plog	0.0001	8.28×10^{80}	-22.15	31790	
	plog	0.0010	3.61×10^{73}	-19.65	30230	
	plog	0.0100	1.31×10^{64}	-16.55	27790	
	plog	0.1000	3.69×10^{53}	-13.14	24810	
	plog	1.0000	1.27×10^{43}	-9.8	21720	
	plog	10.000	1.07×10^{34}	-6.9	19000	
	plog	100.00	1.20×10^{27}	-4.67	16940	
	plog	1000.0	1.09×10^{23}	-3.37	15770	
27	$C_9H_7 + C_3H_3 = R_5C_{12}H_{10}$		5.78×10^{17}	-1.568	455	k
	dup		3.14×10^{19}	-2.163	1195	
28	$C_9H_7 + C_3H_3 = R_5C_{12}H_9 + H$					l
	plog	0.04	1.05×10^{53}	-11.88	28757	
	plog	1.00	1.70×10^{48}	-9.977	26755	
	plog	10.0	3.67×10^{26}	-3.879	28963	
29	$R_5C_{12}H_9 + H (+M) = C_9H_7C_3H_3 (+M)$		1.00×10^{14}	0	0	a
	low		4.40×10^{80}	-18.28	12994	
	tree	0.068	400.7	4135.8	5501.9	
	$H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/$					
30	$R_5C_{12}H_{10} + H = R_5C_{12}H_9 + H_2$		5.60×10^{13}	0	2259	m
31	$R_5C_{12}H_9 = R_5C_{12}H_8 + H$					n
	plog	0.00132	6.28×10^{71}	-18.204	65711	
	plog	0.0132	2.82×10^{61}	-14.813	62790	
	plog	0.132	3.77×10^{47}	-10.443	58072	
	plog	1	7.54×10^{33}	-6.226	52769	
	plog	10	4.44×10^{21}	-2.491	47796	
	plog	100	2.86×10^{13}	0.015	44395	
32	$R_5C_{12}H_9 = A_2R_5 + H$					o
	plog	0.00132	3.68×10^{63}	-15.806	57410	
	plog	0.0132	6.88×10^{51}	-12.098	53279	
	plog	0.132	2.37×10^{38}	-7.917	48317	
	plog	1	9.04×10^{25}	-4.123	43308	
	plog	10	4.13×10^{16}	-1.278	39451	
	plog	100	5.55×10^{12}	-0.065	38028	
33	$R_5C_{12}H_8 + H = A_2R_5 + H$					p
	plog	0.00132	4.94×10^{18}	-1.28	5411	
	plog	0.0132	2.15×10^{22}	-2.28	8429	
	plog	0.132	5.60×10^{26}	-3.47	12818	
	plog	1	1.66×10^{25}	-2.99	13691	
	plog	1.312	5.06×10^{25}	-3.12	14226	
	plog	13.12	2.20×10^{27}	-3.48	19199	
34	$R_5C_{12}H_8 = A_2R_5$					p
	plog	0.04	5.62×10^{81}	-19.36	121500	
	plog	1.00	1.45×10^{45}	-8.90	95999	
	plog	10.0	2.95×10^{31}	-4.97	88465	
35	$C_9H_7 + C_3H_3 = A_2C_2H_3$					q
	plog	0.04	1.82×10^{73}	-18.14	31896	
	plog	1.00	3.16×10^{54}	-12.55	22264	
	plog	10.0	3.88×10^{49}	-11.01	20320	
36	$C_9H_7 + C_5H_6 = C_9H_7C_5H_6$		1.00×10^{-4}	4.2	3400	r

37	$C_9H_8 + C_5H_5 = C_9H_8C_5H_5$		1.00×10^{-4}	4.2	3400	r
38	$C_9H_7C_5H_6 = fC_{13}H_{10}CH_3$		7.00×10^9	1.17	48500	s
39	$C_9H_7C_5H_6 = bC_{13}H_{10}CH_3$		7.00×10^9	1.17	48500	s
40	$C_9H_8C_5H_5 = fC_{13}H_{10}CH_3$		7.00×10^9	1.17	48500	s
41	$C_9H_8C_5H_5 = bC_{13}H_{10}CH_3$		7.00×10^9	1.17	48500	s
42	$fC_{13}H_{10}CH_3 = C_{13}H_{10} + CH_3$		1.52×10^{13}	0.396	32820	t
43	$bC_{13}H_{10}CH_3 = bC_{13}H_{10} + CH_3$		1.52×10^{13}	0.396	32820	t
44	$A_2^1CH_2 + C_2H_2 = bC_{13}H_{10} + H$		3.12×10^{-6}	4.712	1417.5	u
45	$A_2 + C_3H_3 = bC_{13}H_{10} + H$		6.26×10^9	2.61	56500	v
46	$C_9H_7 + C_5H_5 = C_9H_7C_5H_5$					w
	plog	0.04	3.14×10^{174}	-49.43	62602	
	plog	1.00	1.80×10^{188}	-52.62	76380	
	plog	10.0	4.28×10^{174}	-47.91	75125	
47	$C_9H_7 + C_5H_5 = C_9H_6C_5H_5 + H$		5.60×10^{13}	0	2259	x
48	$C_9H_6C_5H_5 + H (+M) = C_9H_7C_5H_5 (+M)$		1.00×10^{14}	0	0	a
	low		4.40×10^{80}	-18.28	12994	
	troe	0.068	400.7	4135.8	5501.9	
	$H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/$					
49	$C_9H_7C_5H_5 + H = C_9H_6C_5H_5 + H_2$		1.12×10^{14}	0	2259	m
50	$C_9H_6C_5H_5 = A_3H$		5.60×10^8	1.31	19100	y
51	$A_3H = A_3 + H$		6.80×10^{11}	0.508	18659	z
52	$C_9H_7C_5H_6 = C_9H_7C_5H_5 + H$		1.55×10^{10}	1.16	45500	aa
53	$C_9H_8C_5H_5 = C_9H_7C_5H_5^b + H$		1.55×10^{10}	1.16	45500	aa
54	$fC_{13}H_9 + CH_3 = fC_{13}H_9CH_3$		6.62×10^{13}	-0.7	-500	bb
55	$bC_{13}H_9 + CH_3 = bC_{13}H_9CH_3$		6.62×10^{13}	-0.7	-500	bb
56	$A_3CH_2 = bC_{13}H_9 + C_2H_2$					cc
	plog	0.013	4.08×10^{134}	-34.08	169130	
	plog	0.130	1.29×10^{112}	-27.5	155360	
	plog	1.000	1.10×10^{89}	-20.82	141680	
	plog	10.00	1.03×10^{55}	-11.23	116580	
	plog	50.00	1.44×10^{13}	0.453	76300	
57	$A_3CH_2 = cC_{15}H_{11}$					g
	plog	0.013	1.12×10^{128}	-32.57	162410	
	plog	0.13	3.23×10^{121}	-30.34	163830	
	plog	1	7.38×10^{95}	-22.95	148280	
	plog	1.5	2.05×10^{13}	0	80700	
	plog	10	3.15×10^{37}	-6.76	99710	
	plog	50	3.60×10^{12}	0.453	76300	
58	$C_9H_7 + C_6H_5 = C_9H_7C_6H_5$					w
	plog	0.013	3.14×10^{174}	-49.43	62602	
	plog	1.000	1.90×10^{188}	-52.62	76380	
	plog	100.0	4.30×10^{174}	-47.91	75125	
59	$C_9H_6C_6H_5 + H (+M) = C_9H_7C_6H_5 (+M)$		1.00×10^{14}	0	0	a
	low		4.40×10^{80}	-18.28	12994	
	troe	0.068	400.7	4135.8	5501.9	
	$H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/$					
60	$C_9H_7C_6H_5 + H = C_9H_6C_6H_5 + H_2$		1.12×10^{14}	0	2259	m
61	$C_9H_6C_6H_5 = cC_{15}H_{11}$		8.40×10^{11}	0.456	42368	[47]
62	$cC_{15}H_{11} = cpC_{15}H_{10} + H$		6.40×10^{12}	0	34800	dd

63	$C_9H_7 + A_1CH_2 = C_9H_7C_7H_7$		8.10×10^{11}	-0.369	1172	[47]
64	$C_9H_7C_7H_7 = C_9H_7CHC_6H_5 + H$		1.30×10^{11}	0.77	4354	[47]
65	$C_9H_7C_7H_7 + H = C_9H_7CHC_6H_5 + H_2$		4.32	3.98	1380	[47]
66	$C_9H_7CHC_6H_5 = C_{10}H_8C_6H_5$		8.10×10^{11}	0.038	11810	[47]
67	$C_{10}H_7C_6H_5 + H = C_{10}H_8C_6H_5$					ee
	plog	0.0263	1.16×10^{41}	-9.51	10830	
	plog	0.1184	2.40×10^{40}	-9.06	11570	
	plog	1.0000	6.82×10^{35}	-7.37	11230	
68	$C_{10}H_6C_6H_5 + H (+M) = C_{10}H_7C_6H_5 (+M)$		1.00×10^{14}	0	0	ff
	low		6.6×10^{75}	-16.3	7000	
	troe	1	0.1	584.9	6113	
	$H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/ C_2H_6/3.0/$					
69	$C_{10}H_7C_6H_5 + H = C_{10}H_6C_6H_5 + H_2$		5.90×10^{11}	0.705	12626	[47]
70	$C_{10}H_6C_6H_5 = C_{16}H_{11}^f$		8.40×10^{11}	0.456	42368	[47]
71	$C_{16}H_{11}^f = C_{16}H_{11}^p$		6.60×10^{11}	0.566	39778	[47]
72	$C_{16}H_{11}^f = fC_{16}H_{10} + H$		6.90×10^{11}	0.548	25832	[47]
73	$C_{16}H_{11}^p = pA_4 + H$		6.80×10^{11}	0.508	18659	[47]
74	$cpC_{15}H_9 + CH_3 = cpC_{15}H_9CH_3$		6.62×10^{13}	-0.7	-500	bb
75	$cpC_{15}H_9 + CH_3 = cpC_{15}H_8CH_3 + H$					c
	plog	0.01	3.03×10^{15}	-0.58	10871	
	plog	0.10	1.23×10^{31}	-1.4	24769	
	plog	1.00	3.23×10^{46}	-5.9	39791	
	plog	10.0	1.49×10^{56}	-9.05	52592	
76	$cpC_{15}H_9CH_3 = cpC_{15}H_8CH_3 + H$					gg
	plog	0.10	1.74×10^{97}	-24.38	116128	
	plog	1.00	5.77×10^{97}	-24.0	122296	
	plog	10.0	1.75×10^{87}	-20.6	120401	
77	$cpC_{15}H_9CH_3 + H = cpC_{15}H_8CH_3 + H_2$		1.30×10^6	2.38	2800	[81]
78	$cpC_{15}H_8CH_3 = pA_4 + H$		9.25×10^{43}	-9.191	55757	hh
	dup		1.98×10^{31}	-6.066	20630	
79	$C_9H_7 + C_9H_8 = C_9H_8C_9H_7$		1.00×10^{-4}	4.2	3400	r
80	$C_9H_8C_9H_7 = C_{17}H_{12}CH_3^b$		7.00×10^9	1.17	48500	s
81	$C_{17}H_{12}CH_3^b = BCF + CH_3$		1.52×10^{13}	0.396	32820	t
82	$bC_{13}H_9 + C_5H_6 = bC_{13}H_9C_5H_6$		1.00×10^{-4}	4.2	3400	r
83	$bC_{13}H_9C_5H_6 = C_{17}H_{12}CH_3^b$		7.00×10^9	1.17	48500	s
84	$bC_{13}H_{10} + C_5H_5 = bC_{13}H_{10}C_5H_5$		1.00×10^{-4}	4.2	3400	r
85	$bC_{13}H_{10}C_5H_5 = C_{17}H_{12}CH_3^b$		7.00×10^9	1.17	48500	s
86	$C_{17}H_{12}CH_3^b = BCF^5CH_3 + H$		6.80×10^{11}	0.508	18659	z
87	$BCF^- + CH_3 = BCF^{11}CH_3$		6.62×10^{13}	-0.7	-500	bb
88	$C_9H_7 + C_9H_7 \Rightarrow C_9H_7C_9H_7$					w
	plog	0.0132	3.14×10^{174}	-49.43	62602	
	plog	1.0000	1.90×10^{188}	-52.62	76380	
	plog	100.00	4.30×10^{174}	-47.91	75125	
89	$C_9H_7C_9H_7 \Rightarrow C_9H_7 + C_9H_7$					w
	plog	0.0132	2.08×10^{70}	-17.55	62254	
	plog	1.0000	1.47×10^{77}	-18.71	73651	
	plog	100.00	1.24×10^{64}	-14.25	72842	
90	$bC_{13}H_9 + C_5H_5 = bC_{13}H_9C_5H_5$					w
	plog	0.0132	3.14×10^{174}	-49.43	62602	

	plog	1.0000	1.90×10^{188}	-52.62	76380	
	plog	100.00	4.30×10^{174}	-47.91	75125	
91	$\text{fC}_{13}\text{H}_9 + \text{C}_5\text{H}_5 = \text{fC}_{13}\text{H}_9\text{C}_5\text{H}_5$					w
	plog	0.0132	3.14×10^{174}	-49.43	62602	
	plog	1.0000	1.90×10^{188}	-52.62	76380	
	plog	100.00	4.30×10^{174}	-47.91	75125	
92	$\text{C}_9\text{H}_6\text{C}_9\text{H}_7 + \text{H} (+\text{M}) = \text{C}_9\text{H}_7\text{C}_9\text{H}_7 (+\text{M})$		1.00×10^{14}	0	0	a
	low		4.40×10^{80}	-18.28	12994	
	troe	0.068	400.7	4135.8	5501.9	
$\text{H}_2/2.0/ \text{H}_2\text{O}/6.0/ \text{CH}_4/2.0/ \text{CO}/1.5/ \text{CO}_2/2.0/$						
93	$\text{C}_9\text{H}_7\text{C}_9\text{H}_7 + \text{H} = \text{C}_9\text{H}_6\text{C}_9\text{H}_7 + \text{H}_2$		1.12×10^{14}	0	2259	[57]
94	$\text{C}_9\text{H}_7\text{C}_9\text{H}_7 + \text{C}_9\text{H}_7 = \text{C}_9\text{H}_6\text{C}_9\text{H}_7 + \text{C}_9\text{H}_8$		3.20×10^{11}	0	15100	ii
95	$\text{C}_9\text{H}_6\text{C}_9\text{H}_7 = \text{C}_{18}\text{H}_{13}^{\text{c}}$		5.60×10^8	1.31	19100	y
96	$\text{C}_9\text{H}_6\text{C}_9\text{H}_7 = \text{C}_{18}\text{H}_{13}^{\text{p}}$		5.60×10^8	1.31	19100	y
97	$\text{C}_{18}\text{H}_{13}^{\text{c}} = \text{C}_{18}\text{H}_{12}^{\text{c}} + \text{H}$					z
	plog	0.04	3.40×10^{10}	0.78	30230	
	plog	1.00	6.80×10^{11}	0.508	18659	
98	$\text{C}_{18}\text{H}_{13}^{\text{p}} = \text{C}_{18}\text{H}_{12}^{\text{p}} + \text{H}$					z
	plog	0.04	3.40×10^{10}	0.78	30230	
	plog	1.00	6.80×10^{11}	0.508	18659	
99	$\text{C}_9\text{H}_7 + \text{C}_9\text{H}_7 = \text{C}_9\text{H}_6\text{C}_9\text{H}_7 + \text{H}$		5.25×10^{14}	-0.853	7254	x
100	$\text{bC}_{13}\text{H}_8\text{C}_5\text{H}_5 + \text{H} (+\text{M}) = \text{bC}_{13}\text{H}_9\text{C}_5\text{H}_5 (+\text{M})$		1.00×10^{14}	0	0	a
	low		4.40×10^{80}	-18.28	12994	
	troe	0.068	400.7	4135.8	5501.9	
$\text{H}_2/2.0/ \text{H}_2\text{O}/6.0/ \text{CH}_4/2.0/ \text{CO}/1.5/ \text{CO}_2/2.0/$						
101	$\text{bC}_{13}\text{H}_9\text{C}_5\text{H}_5 + \text{H} = \text{bC}_{13}\text{H}_8\text{C}_5\text{H}_5 + \text{H}_2$		5.60×10^{13}	0	2259	m
102	$\text{bC}_{13}\text{H}_8\text{C}_5\text{H}_5 = \text{C}_{18}\text{H}_{13}^{\text{c}}$		5.60×10^8	1.31	19100	y
103	$\text{bC}_{13}\text{H}_8\text{C}_5\text{H}_5 = \text{C}_{18}\text{H}_{13}^{\text{p}}$		5.60×10^8	1.31	19100	y
104	$\text{bC}_{13}\text{H}_9 + \text{C}_5\text{H}_5 = \text{bC}_{13}\text{H}_8\text{C}_5\text{H}_5 + \text{H}$		5.25×10^{14}	-0.853	7254	x
	dup		2.00×10^{10}	0.951	15793	
105	$\text{fC}_{13}\text{H}_8\text{C}_5\text{H}_5 + \text{H} (+\text{M}) = \text{fC}_{13}\text{H}_9\text{C}_5\text{H}_5 (+\text{M})$		1.00×10^{14}	0	0	a
	low		4.40×10^{80}	-18.28	12994	
	troe	0.068	400.7	4135.8	5501.9	
$\text{H}_2/2.0/ \text{H}_2\text{O}/6.0/ \text{CH}_4/2.0/ \text{CO}/1.5/ \text{CO}_2/2.0/$						
106	$\text{fC}_{13}\text{H}_9\text{C}_5\text{H}_5 + \text{H} = \text{fC}_{13}\text{H}_8\text{C}_5\text{H}_5 + \text{H}_2$		5.60×10^{13}	0	2259	m
107	$\text{fC}_{13}\text{H}_8\text{C}_5\text{H}_5 = \text{C}_{18}\text{H}_{13}^{\text{t}}$		5.60×10^8	1.31	19100	y
108	$\text{C}_{18}\text{H}_{13}^{\text{t}} = \text{C}_{18}\text{H}_{12}^{\text{t}} + \text{H}$		6.80×10^{11}	0.508	18659	z
109	$\text{fC}_{13}\text{H}_9 + \text{C}_5\text{H}_5 = \text{fC}_{13}\text{H}_8\text{C}_5\text{H}_5 + \text{H}$		5.25×10^{14}	-0.853	7254	x
	dup		2.00×10^{10}	0.951	15793	

[#] The rate constants are given in the form of $k = A \cdot T^n \cdot e^{-E_a/RT}$, where A has the units of cm, mol and s; T has the unit of K; E_a has the unit of cal/mol.

a Rate constant analogized to $\text{C}_5\text{H}_5 + \text{H} = \text{C}_5\text{H}_6$ in JetSurf 2.0 model [82].

b Rate constant analogized to $\text{C}_5\text{H}_6 + \text{H} = \text{C}_5\text{H}_5 + \text{H}_2$, calculated by Robinson et al. [34].

c Rate constant analogized to $\text{C}_5\text{H}_5 + \text{CH}_3 = \text{C}_5\text{H}_5\text{CH}_2 + \text{H}$, calculated by Sharma and Green [51].

d Rate constant analogized to $\text{C}_5\text{H}_5 + \text{C}_2\text{H}_2 = \text{C}_7\text{H}_6 + \text{H}$ calculated by Da Silva et al. [83].

e Rate constant analogized to $\text{A}_1\text{CH}_2 = \text{C}_7\text{H}_6 + \text{H}$ calculated by Polino et al. [84].

f Rate constant analogized to $\text{C}_7\text{H}_6 + \text{H} = \text{A}_1\text{CH}_2$ calculated by Cavallotti et al. [85].

g Rate constant analogized to $\text{A}_1\text{CH}_2 = \text{cC}_7\text{H}_7$ estimated in the model of Yuan et al. [56].

h Rate constant analogized to $\text{cC}_7\text{H}_7 + \text{H} = \text{A}_1\text{CH}_2 + \text{H}$ calculated by Fascella et al. [79].

i Rate constant analogized to $\text{cC}_7\text{H}_7 + \text{H} = \text{A}_1^- + \text{CH}_3$ calculated by Fascella et al. [79].

j Rate constant analogized to $\text{C}_5\text{H}_5 + \text{C}_2\text{H}_2 = \text{cC}_7\text{H}_7$ calculated by Da Silva et al. [83].

k Rate constant taken equal to $\text{A}_1\text{CH}_2 + \text{C}_3\text{H}_3 = \text{A}_1\text{CH}_2\text{C}_3\text{H}_3$ calculated by Matsugi and Miyoshi [45].

l Rate constant taken equal to $A_1CH_2 + C_3H_3 = C_{10}H_9 + H$ in the model of Matsugi and Miyoshi [57].
 m Rate constant analogized to $C_5H_5C_5H_5 + H = C_5H_5C_5H_4 + H_2$ calculated Matsugi and Miyoshi [57].
 n Rate constant taken equal to $C_9H_6CH_3 = C_9H_6CH_2 + H$ calculated by Matsugi and Miyoshi [45].
 o Rate constant taken equal to $C_9H_6CH_3 = A_2 + H$ calculated by Matsugi and Miyoshi [45].
 p Rate constant taken equal to the isomerization of $C_9H_6CH_2$ and A_2 calculated by Matsugi and Miyoshi [45].
 q Rate constant analogized to $C_5H_5 + C_3H_3 = A_1C_2H_3$ in the model of Yuan et al. [42,55].
 r Rate constant analogized to $C_5H_5 + C_5H_6 = C_5H_6C_5H_5$ calculated by Kislov et al. [86].
 s Rate constant taken equal to the controlling step of the isomerization from $C_5H_6C_5H_5$ to $C_9H_6CH_3$, calculated by Kislov et al. [86].
 t Rate constant taken equal to $C_6H_{10}CH_3 = C_6H_{10} + CH_3$ in the model of Narayanaswamy et al. [87].
 u Rate constant analogized to $A_1CH_2 + C_2H_2 = C_9H_8 + H$ by the calculation of Vereecken and Peeters [88].
 v Product of this reaction changes to benzo-indene, it is proposed to form fluorene in the model of Yuan et al. [56].
 w Rate constant analogized to $C_5H_5 + C_5H_5 = C_5H_5C_5H_5$ calculated by Matsugi and Miyoshi [57].
 x Rate constant analogized to $C_5H_5 + C_5H_5 = C_5H_5C_5H_4 + H$ calculated by Cavallotti et al. [46].
 y Rate constant analogized to $C_5H_5C_5H_4 = C_{10}H_9$ calculated by Kislov et al. [43].
 z Rate constant analogized to $C_{16}H_{11} = pA_4 + H$ calculated by Sinha et al. [47].
 aa Rate constant analogized to $C_5H_6C_5H_5 = C_5H_5C_5H_5 + H$ calculated by Wang et al. [49].
 bb Rate constant analogized to $C_5H_5 + CH_3 = C_5H_5CH_3$ calculated by Sharma and Green [51].
 cc Rate constant analogized to $A_1CH_2 = C_5H_5 + C_2H_2$ estimated in the model of Yuan et al. [56].
 dd Rate constant analogized to $C_5H_7 = C_5H_6 + H$ estimated in the model of Gueniche et al. [89].
 ee Rate constant analogized to $C_6H_5C_6H_5 + H = C_6H_6C_6H_5$ estimated in the model of Wang and Frenklach [14].
 ff Rate constant analogized to $A_1 + H = A_1$ estimated in the model of Wang and Frenklach [14].
 gg Rate constant analogized to $C_5H_5CH_3 = C_5H_5CH_2 + H$ calculated by Sharma and Green [51].
 hh Rate constant analogized to $C_5H_5CH_2 = A_1 + H$ in the model of Harper et al. [90].
 ii Rate constant analogized to $C_5H_5C_5H_5 + C_5H_5 = C_5H_5C_5H_4 + C_5H_6$ calculated by Matsugi and Miyoshi [57].

193

194 4.1 Indene (C_9H_8) decomposition reactions

195 4.1.1. Indenyl (C_9H_7) formation

Indenyl radical is the most critical intermediate in the growth of PAH from indene. Indenyl may
 be formed *via* the combination of smaller aromatic species [10,79]; however, it is largely derived from
 indene. H-elimination (R1) and H-abstraction (R2) are the dominant reactions in the consumption of
 indene, both resulting in the formation of indenyl. As shown in **Scheme 1**, C-H bond energy of the 1°
 site is 1.2 kcal/mol lower than its weakest C-C bonds. Unimolecular C-H decomposition should be
 favored compared to the unimolecular C-C bond fission. Laskin and Lifshitz [62] estimated the rate
 constant for C-H bond dissociation of indene (R1) to be $1.1 \times 10^{15} e^{-77000/RT} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, which is
 pressure-independent. However, different values were adopted in later models [7,8,66,77]. For
 example, Lifshitz et al. [66] and Pousse et al. [77] also considered R1 to be pressure-independent and
 temperature-independent; they estimated the rate constant to be 6.0×10^{13} and $1.0 \times 10^{14} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,
 respectively. Blanquart et al. [7] proposed R1 in its reverse direction and recommended its value to be
 same as that of cyclopentadiene, $1.73 \times 10^{68} T^{-15.16} e^{-116372/RT} \text{ s}^{-1}$. Laskin and Lifshitz [62] evaluated the
 rate constant of R2 as $1.0 \times 10^{14} e^{-5500/RT} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ according to the measurements of

cyclopentadiene decomposition by Roy et al. [91]. In some literature models, this rate constant was also proposed in analogy to H-abstraction reactions of other alkenes [3,92,93]. In this study, we adopt the rate constants of R1 and R2 analogously to those of cyclopentadiene. Here, R1 is taken from the H-elimination of cyclopentadiene in Jet-surf 2.0 model [82], which was also adopted in some other PAH models [8,56,77]. The rate constant of R2 is referred to the calculations of Robinson and Lindstedt [34] on cyclopentadiene.

Scheme 1 (a) C-H and (b) C-C bond energies of indene, calculated at 298 K. Unit: kcal/mol.

4.1.2. Indenyl (C_9H_7) and indanyl (C_9H_9) decomposition reactions

Indenyl radical is very difficult to decompose at intermediate temperatures (~ 1200 K) compared to other fuel radicals [62,94,95]. According to the models of Yuan et al. [56], Slavinskaya et al. [39], and Matsugi and Miyoshi [57], three decomposition pathways of indenyl are included in present model, forming cyclopentadienyl + butadiyne, benzyne + propargyl, and fulvenallenyl + acetylene.

H-addition reactions of indene (R3-R4) form two indanyl isomers ($C_9H_9^1$: radical on 1° site, $C_9H_9^2$: radical on 2° site). The sub-mechanism of indanyl radical was studied by Pousse et al. [77]. Here, we include that part of their model in the present model. Further reactions of two indanyl isomers will be analyzed in the discussion section (**Section 5.1.2**).

4.2 PAH formation via indenyl reactions

PAH formation mechanism is too complicated to be fully reviewed in this section. We will limit to the specific molecule of this study. C_9H_7 has three isomers, labelled $C_9H_7^1$ (indenyl), $C_9H_7^2$ and $C_9H_7^3$. However, considering the high energy barrier (> 100 kcal/mol, see *SMM3*) of H-shift from indenyl to other isomers ($C_9H_7^2$ and $C_9H_7^3$), indenyl is the most favorable precursor of further PAH

232 growth pathways. Hence, the formation pathways of C₁₀-C₁₈ PAHs in this work are considered based
233 on the indenyl radical.

234 **4.2.1. C₁₀ aromatic species**

235 The mechanism of C₁₀ species has been studied in detail in literature [66,78,96]. It mainly includes
236 the reactions of methyl-indene isomers, C₁₀H₉ radicals, naphthalene (C₁₀H₈), describing the conversion
237 from indenyl to naphthalene *via* the addition of a methyl radical. Reactions of methyl-indene were
238 considered to be rather important pathway in naphthalene formation [53]; therefore, we included all
239 three methyl-indene (C₁₀H₁₀) isomers in the present model. As calculated by Dubnikova and Lifshitz
240 [78], the isomerization reactions of C₁₀H₁₀ and C₁₀H₉ species are very quick. 1,5 H-shift could also
241 easily occur in cyclopentadienyl structure [46,51], thus 3-methyl-indene could be a more favorable
242 intermediate due to its lower energy among the three isomers [78]. As shown in Table 1, combination
243 of indenyl and methyl radicals forms 1-methyl-indene (R5). It later isomerizes to 2- and 3-methyl-
244 indene. Further decomposition and H-abstraction reactions of methyl-indene isomers produce various
245 C₁₀H₉ radicals. Well-skipping reaction between indenyl and methyl may directly form C₉H₆³CH₃
246 radical (R16). According to the calculations of Dubnikova and Lifshitz [78], only three C₁₀H₉ radicals,
247 3-methyl-1-indenyl (C₉H₆³CH₃), 1-indenyl-methyl (C₉H₇¹CH₂) and 2-indenyl-methyl (C₉H₇²CH₂), are
248 considered to be favorable in the subsequent isomerization reactions. Further C₁₀H₉ isomerization
249 reactions (R6-R13) yield α- and β-naphthyl radicals (aC₁₀H₉ and bC₁₀H₉), which are naphthalene
250 (C₁₀H₈) precursors (R14 and R15). In addition, ipso-reactions of methyl-indene isomers yield methyl
251 and indene (R17-R19).

252 **4.2.2. C₁₁ aromatic species**

253 We considered two groups of species for C₁₁ aromatics: ethynyl-indene and methyl-naphthalene.
254 The combination between indenyl and acetylene is proposed in this model to form naphthyl-methyl
255 (A₂¹CH₂) and benzo-cycloheptatrien-5-yl (cC₁₁H₉) radicals. Ethynyl-indene and methyl-naphthalene
256 are then formed in a few elementary steps, as shown in Table 1. R20-R26 are analogized to those of

257 cyclopentadienyl [64] in the present model; their rate constants are taken from the calculations in
258 literature [64,79,83,84].

259 4.2.3. C_{12} aromatic species

260 Two $C_{12}H_8$ isomers are considered in the present model, acenaphthylene (A_2R_5) and ethynyl-
261 naphthalene (A_2C_2H). Acenaphthylene, having fused six- and five-member rings, is an important
262 intermediate in PAH growth. According to the literature models, it is either proposed to be formed
263 through the combination of indenyl and propargyl [7,10,97] or the cyclization of naphthyl-2-vinyl
264 radical ($A_2C_2H_2$) [14,16]. A global rate constant used in literature models [8,56] is referred to the
265 estimation of Blanquart et al. [7], which was based on the assumption that indenyl radical gets a benzyl-
266 like structure by its reaction with propargyl (see the part of molecule highlighted in red in **Scheme 2**).
267 The benzyl-like part in indenyl is added by propargyl, and then cyclizes to form another benzene ring
268 inbetween the six- and five-member rings of indene. As a result, this reaction consumes two relatively
269 less reactive radicals (C_9H_7 and C_3H_3), but produces two H-atoms that are much more active. Recent
270 calculations of Long et al. [48] for the combination of two cyclopentadienyl radicals and Sinha et al.
271 [47] for the combination of indenyl and benzyl showed that a necessary H-loss step (*via* H-abstraction
272 or H-elimination reactions) from $|R'-R|$ to $|R'-R|^*$ radical (R and R' are functional groups, * is a radical
273 label) should be considered in the model, particularly at relatively low temperatures. This approach
274 will effectively adjust the over-estimation of the system reactivity by the global reaction, since it
275 consumes an extra radical in H-abstraction reaction of $|R'-R|$ (three radicals in and one out). Therefore,
276 in this work, we proposed a multi-step scheme for the addition of propargyl to indenyl (R27-34) and
277 analogized to that of benzyl [9,45,56,57] but also included a necessary H-abstraction reaction step
278 (R30). Detailed reaction process is shown in **Scheme 2**.

Scheme 2 Reaction scheme proposed for $C_9H_7 + C_3H_3$. Solid arrows represent elementary reaction steps, dashed arrows represent multiple reaction steps. Blue dashed arrow highlights the key H-abstraction reaction step.

The addition of acetylene on naphthyl radical can produce naphthyl-2-vinyl radical. It either cyclizes to acenaphthylene or forms ethynyl-naphthalene *via* C-H bond cleavage. Herein, we propose another vinyl-naphthalene formation reaction *via* the combination of indenyl and propargyl radical (R35), competing with the route proposed for acenaphthylene. This is analogized to the styrene formation reaction by cyclopentadienyl and propargyl [10,40,98].

4.2.4. C_{13} aromatic species

Benz[g]indene, benz[f]indene and fluorene are typical $C_{13}H_{10}$ PAHs that can be formed *via* the combination of indenyl and cyclopentadienyl radicals [50]. H-elimination reactions of these molecules yield benz[g]indenyl, benz[f]indenyl and fluorenyl radicals, which are also cyclopentadienyl-like radicals but have tricyclic rings. We proposed two molecular structure groups for $C_{13}H_{10}$ and $C_{13}H_9$ species in the present model: one group represents the benz-indene isomers ($bC_{13}H_{10}$) and their radicals ($bC_{13}H_9$) while the other group represents fluorene ($fC_{13}H_{10}$) and fluorenyl radical ($fC_{13}H_9$). Benz-indenyl is treated separately from fluorenyl because the chemical reactivity of the five-member ring in this molecule is impacted by one benzene ring on its single side whilst that of fluorenyl is impacted on its both sides. Fluorenyl would be more difficult to undergo internal ring rearrangement than benz-indenyl radical after its addition reactions since the Pi-bond of fluorenyl is stronger than the double bond of benz-indenyl. Therefore, we consider benz-indenyl to be more active in PAH growth. In addition, fluorenyl and benz-indenyl radicals produce very different large PAHs through subsequent

301 reactions with same intermediates. However, benz[g]indenyl and benz[f]indenyl form similar products
 302 in further reactions, are thus lumped.

303 The combination of indenyl and cyclopentadienyl [50] could be similar to that of two
 304 cyclopentadienyls [43,48]. However, the reactions of $C_9H_7 + C_5H_6$ and $C_9H_8 + C_5H_5$ are slightly
 305 different from $C_5H_5 + C_5H_6$ because of the non-symmetrical structures of $C_9H_7C_5H_6$ and $C_9H_8C_5H_5$
 306 (see their structures in **Scheme 3**). These will either eliminate an H-atom forming $C_9H_7C_5H_5$ or
 307 undergo isomerization steps forming $fC_{13}H_{10}CH_3$ and $bC_{13}H_{10}CH_3$ radicals. The products of these two
 308 channels are similar, mainly fluorene and benzo-indene. We propose the following scheme (R36-43)
 309 based on the calculations of Mulholland et al. [50]; rate constants are analogized to the similar reactions
 310 between cyclopentadienyl and cyclopentadiene [86].

311

312 **Scheme 3** Reaction scheme proposed for $C_9H_8 + C_5H_5$ and $C_9H_7 + C_5H_6$. Solid arrows represent
 313 elementary reaction steps; dashed arrows represent reactions with multiple steps.

314 In addition to the reactions suggested by Mulholland et al. [50], we also propose a formation
 315 pathway of benz-indene from naphthylmethyl (R44), similar to the formation of indene from the
 316 combination of benzyl and acetylene [88]. For the combination of propargyl and naphthalene (R45)
 317 [19,56], we recommend its product to be benz-indene instead of fluorene because the addition of

propargyl is more likely to create a fused five-member ring on one side than in the middle of naphthalene.

4.2.5. C_{14} aromatic species

$C_{14}H_{10}$ and $C_{14}H_{12}$ are the main groups of C_{14} PAHs considered in the kinetic models. Anthracene and phenanthrene are the $C_{14}H_{10}$ isomers identified in previous studies, and are typical tricyclic aromatic species. In our model, we lumped these two isomers, since they have very similar growth pathways and yield products with similar structures. Beside HACA formation pathways for $C_{14}H_{10}$ PAHs [3,14], we propose the combination of indenyl and cyclopentadienyl (R46-51) to be an efficient route [50] (see **Scheme 3**). The rate constants of R46-51 are again analogized to that of cyclopentadienyl (see Table 1).

For $C_{14}H_{12}$ species, Yuan et al. [56] and Matsugi and Miyoushi [57] proposed stilbene to be a possible structure in their modeling studies of toluene combustion. However, benzyl radical concentration is much less than indenyl in the present study; stilbene is thus not that important compared to the products derived from indenyl reaction sequences. Therefore, we assumed $C_{14}H_{12}$ to be methyl-benzindene or methyl-fluorene formed through the combination of methyl and benz-indenyl or fluorenyl (R54-55). Further reactions of both species can form phenanthrene, similar to the transformation from methyl-cyclopentadiene to benzene [51].

4.2.6. C_{15} aromatic species

Methyl-phenanthrene (A_3CH_3) can be formed *via* many pathways; simplest one is the methyl addition to phenanthrene. When methyl-phenanthrene loses an H-atom, phenanthrenyl-methyl radical (A_3CH_2) is formed. This radical can also be produced by the combination of benz-indenyl and acetylene (R52), which is similar to the conversion from cyclopentadienyl to benzyl. Cyclization of phenanthrenyl-methyl radical yields another radical (R57), see $cC_{15}H_{11}$ in **Scheme 4**. Thereafter, 4H-cyclopenta[def]phenanthrene ($cpC_{15}H_{10}$) can be formed *via* β -scission of its C-H bond (R62). We also proposed $cpC_{15}H_{10}$ to be formed through the combination of indenyl and phenyl. As shown in **Scheme 4**, 1-phenyl-1H-indene ($C_9H_7C_6H_5$) loses an H-atom to form $C_9H_6C_6H_5$ radical. It then isomerizes to

344 $cC_{15}H_{11}$ radical via seven-member-ring structure intermediates. A brief reaction scheme (R58-61) is
 345 shown in Table 1 with estimated rate constants. Opening of double bonds in $C_9H_7C_6H_5$ and further
 346 cyclization is considered negligible, as shown by the red cross in **Scheme 4**.

347

348 **Scheme 4** Reaction scheme proposed for $C_9H_7 + C_6H_5$. Solid arrows represent elementary reaction
 349 steps; dashed arrows represent reactions with multiple steps.

350 4.2.7. C_{16} aromatic species

351 $C_{16}H_{10}$ has at least four tetracyclic isomers that can be detected and should be considered in the
 352 PAH model; these are pyrene, fluoranthene, acephenanthrylene and aceanthrylene. According to the
 353 previous studies, pyrene is proposed to be the dominant isomer among these [3-5,7,9,10,57]. However,
 354 recent atomic force microscopy measurements on PAHs has shown a significance of the five-member-
 355 ring in their molecular structures [99]. Therefore, acephenanthrylene and aceanthrylene could still be
 356 important in PAH formation, although they cannot be easily distinguished from other $C_{16}H_{10}$ isomers.
 357 The sub-mechanisms of acephenanthrylene and aceanthrylene are not included in the present model
 358 due to the lack of their kinetic data. These sub-mechanisms are not closely related to indenyl reactions
 359 and could be completed in a future study. We added the reaction of indenyl and benzyl in the present
 360 model (R63-R73 in Table 1) for pyrene (pA_4) and fluoranthene ($fC_{16}H_{10}$), which are adopted from the
 361 quantum chemical calculations of Sinha et al. [47]. After the combination of indenyl and benzyl (R63),
 362 the product $C_9H_7C_7H_7$ undergoes several reaction steps (R64-R67) to form phenyl-naphthalene
 363 ($C_{10}H_7C_6H_5$). The following reaction sequence of $C_{10}H_7C_6H_5$ (R68-R73) is the same as the reaction
 364 pathway of naphthyl and phenyl combination. The addition reaction of methyl to $cpC_{15}H_9$ is also
 365 considered a potential pyrene formation pathway (R74-R78). Besides these routes, we propose the

addition of propargyl on fluorenyl to yield fluoranthene, analogized to the addition of propargyl on benz-indenyl [97].

4.2.8. C_{17} aromatic species

C_{17} PAH species have not been detailed in previous studies [11,100,101]; particularly their specific formation pathways and carbon growth reactions are not described adequately. Previous quantum chemical calculations pointed out that the combination of indenyl and indene can form C_{17} and C_{18} species [65]. Three benzo[fluorene] isomers may be formed in this reaction scheme, benzo[b]fluorene (BCF) is emphasized as a major isomer [65]. As shown in **Scheme 5a**, Kislov et al. [86] calculated a series of $C_{10}H_{11}$ isomerization reactions from 3a,4,7,7a-tetrahydro-1*H*-4,7-methano-indenyl (INT1) to 7-methyl-7,7a-dihydro-1*H*-7a-indenyl (INT3) after the combination of cyclopentadienyl and cyclopentadiene. β -Scission of INT3 preferentially produces indene rather than methyl-indene because of the weaker dissociation energy of C-C bond than C-H bond. A modified scheme for $C_9H_8 + C_9H_7$ (R79-R81 in Table 1) is adopted in the present model analogously to $C_5H_6 + C_5H_5$ reactions, as shown in **Scheme 5b**.

Scheme 5 Reaction schemes (a) for $C_5H_6 + C_5H_5$ calculated by Kislov et al. [86], (b) proposed here for $C_9H_8 + C_9H_7$. Solid arrows represent elementary reaction steps; broad arrows represent reactions with multiple steps.

Benzofluorene pathways *via* the combination of benz-indene and cyclopentadienyl or benz-indenyl and cyclopentadiene (R82-R85) are also considered in the present model, following the repetitive chemical reactions of cyclopentadienyl and indenyl (**Scheme 5**).

389 4.2.9. C_{18} aromatic species

390 We consider three kinds of C_{18} PAH species in the present model, with formulae of $C_{18}H_{14}$, $C_{18}H_{12}$
391 and $C_{18}H_{10}$. $C_{18}H_{14}$ could be 5-methyl-benzofluorene (BCF^5CH_3), formed by the β -scission of
392 $C_{17}H_{12}CH_3^b$ (R86) [65]. Another methyl-benzofluorene isomer, labeled as 11-methyl-benzofluorene
393 ($BCF^{11}CH_3$), is the product of the addition of methyl and benzo-fluorenyl radicals (R87). Bi-indene
394 isomers are dominant $C_{18}H_{14}$ species [63,65]. In the previous studies of cyclopentadienyl combination
395 [46,48], the intermediate 1,1- $C_5H_5C_5H_5$ ([1,1'-bi(cyclopentane)]-2,2',4,4'-tetraene) can easily
396 isomerize to other structures, such as 2,2- $C_5H_5C_5H_5$, 2,3- $C_5H_5C_5H_5$ and 3,3- $C_5H_5C_5H_5$. Bi-indene has
397 similar isomers and reaction network. We lumped all bi-indene isomers as 3,3-bi-indene in order to
398 simplify the present model because all isomers have very similar further reactions [48]. This is the
399 same strategy adopted in the model of Yuan et al. for cyclopentadienyl combination reactions [56].
400 The related reactions of indenyl combination (R88 and R89 in Table 1) are analogized to those of
401 cyclopentadienyl, as shown in **Scheme 6**. Furthermore, the combinations of $C_{13}H_9$ isomers and
402 cyclopentadienyl produce other $C_{18}H_{14}$ isomers (R90 and R91), fluorenyl-cyclopentadiene
403 ($fC_{13}H_9C_5H_5$) and benzindenyl-cyclopentadiene ($bC_{13}H_9C_5H_5$).

404 Three $C_{18}H_{12}$ isomers, chrysene ($C_{18}H_{12}^c$), benzo[c]phenanthrene ($C_{18}H_{12}^p$), and triphenylene
405 ($C_{18}H_{12}^t$), are considered in the present model. Among these, chrysene is a typical $C_{18}H_{12}$ PAH that
406 has been frequently studied in previous models [3,7,14,15,18,19,39,55,56]. $C_9H_7C_9H_7$ eliminates an
407 H-atom yielding $C_9H_6C_9H_7$ radical, and it isomerizes to hydrochrysenyl ($C_{18}H_{13}^c$, R95) or
408 hydrobenzo[c]phenanthrenyl ($C_{18}H_{13}^p$, R96). The β -scission reactions of $C_{18}H_{13}^c$ and $C_{18}H_{13}^p$ form
409 chrysene and benzo[c]phenanthrene (R97 and R98), respectively. Another formation channel of
410 $C_9H_6C_9H_7$ radical is the well-skipping reaction of two indenyl radicals (R99). The proposed formation
411 pathway for chrysene is shown in **Scheme 6b**, while similar reactions for benzo[c]phenanthrene are
412 omitted.

Scheme 6 Reaction schemes (a) for $C_5H_5 + C_5H_5$, (b) proposed for $C_9H_7 + C_9H_7$. Solid arrows represent elementary reaction steps; dash arrows represent reactions with multiple steps.

Subsequent reactions of benzindenyl-cyclopentadiene ($bC_{13}H_9C_5H_5$) may also form chrysene and benzo[c]phenanthrene (R100-R104). Slightly different reactions of fluorenyl and cyclopentadienyl yields triphenylene (R105-R109).

4.2.10. PAHs beyond 18 C-atoms

Since these species are not directly observed in the current experiments, we have provided detailed information of this part in **Section 3** of *SMM2*. Simple reaction schemes are included for some C_{19} and C_{20} species, as collected in Table S2. Self-combination of large resonantly stabilized radicals were considered for larger PAHs in previous studies [59,61]. In the present model, global reactions are applied for these pathways.

4.3 Thermodynamic and transport data

Thermodynamic and transport data of C_0 – C_6 species used in this work are taken from literature models [56,70], and those of aromatic species are taken from references [7,14,57,97,102]. Thermo data of new species added in the present model are calculated by group-additivity method [103-105].

5. Model validation

In this section, the present model is validated against the current flow reactor experimental data and the shock tube data of Laskin and Lifshitz [62]. Numerical simulations of flow reactor and shock

434 tube was performed with OpenSMOKE++ [106]. Energy equation was not solved in the flow reactor;
 435 instead temperature profiles measured in the experiment were used as input parameters (see *SMMI*).
 436 Shock tube was modelled as an adiabatic batch reactor, and the residence time was set to 1.7 ms
 437 according to the experimental method reported in [107]. The main dissociation channels of indene and
 438 ring expansion routes from indenyl radical are illustrated based on the kinetic analysis of the present
 439 model.

440 5.1 Indene pyrolysis in flow reactor

441 Dozens of pyrolysis products were detected in the flow reactor pyrolysis experiments of indene,
 442 and their mole fraction profiles are plotted as a function of reaction temperature. The experimental and
 443 simulated mole fraction profiles of pyrolysis species are shown in Figs. 1-4. In general, the current
 444 model can adequately capture the decomposition or formation temperature windows of the observed
 445 pyrolysis species, and the quantitative agreement between the experiments and model is quite
 446 reasonable. Rate of production (ROP) analysis and sensitivity analysis are used to provide insights into
 447 the chemistry of indene decomposition and aromatics growth.

448
 449 **Figure 1** Measured mole fraction profiles of indene (C_9H_8) and its main decomposition products in
 450 a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots
 451 represent the uncertainty of the measurements. Lines are predictions of the present model.

Figure 2 Mole fraction profiles of small intermediates measured in indene pyrolysis in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. The blue circles in (c) and (d) are the mole fractions of propargyl and 5-vinylidene-1,3-cyclopentadiene at 30 Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines are the predictions of the present model. Experimental data and simulations of species with small concentrations are scaled with a common factor.

Figure 3 Mole fraction profiles of dominant (common) PAHs measured in indene pyrolysis in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines indicate the model predictions.

Figure 4 Mole fraction profiles of uncommon PAHs measured in indene pyrolysis in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines indicate the model predictions.

5.1.1 Primary decomposition of indene

Indene consumption profiles are presented in Fig. 1(a) and compared with simulation results. Only 50% of indene conversion is observed during the experiments at ~ 1300 and 1500 K for 30 and 760 Torr respectively. Higher conversions of indene at higher temperatures were not measured due to the increasing influence of soot on the sampling process. The present model captured the temperature dependencies of indene consumption at both pressures. ROP analyses were performed under two different conditions at an indene conversion of 17.5%. The reaction networks in the decomposition of indene at both pressures are plotted in Fig. 5. The dominant product of indene decomposition is indenyl radical which accounts for more than 70% of indene consumption. The low C-H bond energy favors a competitive selectivity of H-elimination reaction compared to C-C bond dissociation reaction in unimolecular consumption channels. At higher pyrolysis pressure, molecules collide more frequently, so bimolecular H-abstraction reaction takes dominance in indene consumption.

Figure 5 Reaction flux analysis of indene decomposition at 17.5% conversion. Arrows indicate reaction steps; the numbers indicate the conversion ratios of each step at 30 (black) and 760 Torr (red).

Indanyl and 5-vinylidene-1,3-cyclopentadiene (C₇H₆) are minor indene consumption products. Rate of production (ROP) analysis in Fig. 5 shows that two indanyl radicals account for ~ 20% of the total carbon flux from indene, where the contribution of each channel does not change much as pressure increases. Unimolecular decomposition yielding C₇H₆ contributes less than 1% to the total indene consumption.

Sensitivity analysis for indene consumption is shown in Fig. 6. The mole fraction of indene is sensitive to the high-pressure limit of R1 at both pressures. The low-pressure limit of R1 is more sensitive at 30 Torr, while R2 is more sensitive at 760 Torr. H-addition reaction (R3) plays a negative

effect on indene decomposition at higher pressure since it has a competition with R2 for H-atom consumption.

Figure 6 Normalized sensitivity coefficient of indene consumption, performed at an indene conversion of 17.5% at 30 and 760 Torr. Only the most sensitive four reactions are listed. HPL and LPL are high- and low-pressure limits of R1.

5.1.2 Decomposition of C_9 intermediates

ROP analysis (performed at 17.5% indene conversion) illustrates that indenyl decomposition is negligible, though three unimolecular dissociation pathways are included in the present model. Indenyl combination channels consumes 71% and 98% at 30 and 760 Torr, respectively. It should also be noted that the rate constants of indenyl dissociation reactions are estimated in literature models [39,56,57]. However, these reactions may impact PAH formation through the carbon flux competition of indenyl. Therefore, accurate quantum calculations of indenyl decomposition are required to adequately illustrate the kinetics of indenyl radical.

As shown in Fig. 5, 2-indanyl (C_9H_9^2), isomerized from 1-indanyl (C_9H_9^1), later opens its five-member ring to form phenyl-allyl ($\text{C}_6\text{H}_5\text{C}_3\text{H}_4$). At 30 Torr, indanyl mainly isomerizes to phenyl-allyl. When reaction pressure raises, more indanyl reacts with indenyl and goes back to indene. Further isomerization and decomposition of phenyl-allyl contributes to benzyl (~ 60%), phenyl (~ 20%), cyclopentadienyl (<15%) and phenyl-acetylene (<6%). They are precursors of toluene, cyclopentadiene and benzene. Model predictions of these species are presented in Fig. 1 and 2.

513 **5.1.3 Formation of small intermediates**

514 Small intermediates, particularly C₂-C₅ hydrocarbons, are formed through various pathways *via*
515 multi-elementary reaction steps. 5-Vinylidene-1,3-cyclopentadiene formed *via* the unimolecular
516 decomposition of indene may lead to C₇H₇ or C₇H₅ radicals. C₇H₅ radical is mostly formed by the
517 decomposition of C₇H₆; it further decomposes to C₄H₂, C₃H₃ and C₂H₂ [108] or contributes in PAH
518 formation via combination reactions. Isomerization and dissociation of phenyl-allyl impact the
519 formation of small intermediates, such as propargyl, allene, propyne, acetylene and vinyl-acetylene.
520 Propargyl combines with cyclopentadienyl to form styrene which is a major formation pathway of
521 styrene at 760 Torr. At 30 Torr, styrene is mainly formed *via* a complicated H-addition pathway from
522 indanyl where phenyl-allyl and phenyl-propyl radicals are key intermediates in this process.

523 Model predictions of these small species are shown in Fig. 2. Only the data at 30 Torr are presented
524 for active species, such as C₇H₆, C₇H₅, C₅H₅ and C₃H₃, since the concentration of these species is too
525 low to be detected at 760 Torr. The mole fractions of small intermediates, such as allene, propyne,
526 vinyl-acetylene and butadiyne, decrease as the pressure increases. It is because the formation of these
527 species is more or less controlled by the isomerization of indanyl to phenyl-allyl, as shown in Fig. 5

528 **5.1.4. Formation of common PAHs**

529 Although the dominant contributor to PAH growth would be indenyl radical (**Sections 5.1.4** and
530 **5.1.5**), we still want to know if other cyclopentadienyl-like or benzyl-like radicals have any
531 contribution in this process (See **Section 5.1.6**). One point that needs to be clarified for the experiments
532 of this work is that the mole fractions of PAHs are not calculated for every isomer due to their close
533 ionization energies. As introduced in the experimental method **Section 2** [68,80], additional
534 measurements need to be performed at photon energies between the ionization energies of every two
535 neighboring isomers. Due to the close ionization energies between isomers, the photon energy applied
536 in the measurement would be very close to the ionization energy of the target isomer. In this case, the
537 cross-section of this target isomer at the applied photon energy is very small, so that its signal would
538 be easily influenced by the uncertainties of its isomers with larger cross sections. In general, this

539 treatment may introduce large random uncertainty in the mole fraction values through measurement
 540 and mathematical process. Therefore, we instead decided to use one summed mole fraction of all PAH
 541 isomers with the same chemical formula when comparing with modelling results.

542

543 **Figure 7** ROP analysis performed for C₁₇ and C₁₈ species at 70% indene conversion. The blue frame
 544 highlights larger RSR generated by indenyl radical. Numbers beside the arrows are the
 545 contributions of this reaction step in the consumption of the precursors. Black and red
 546 colors separate 30 and 760 Torr conditions, respectively. Bold arrows indicate those
 547 reaction steps that consume > 99.5% of the precursors.

548 PAH species commonly discussed in previous PAH studies are presented in Fig. 3; these are
 549 C₁₈H₁₄, C₁₈H₁₂, C₁₆H₁₀, C₁₄H₁₀, C₁₂H₈ and C₁₀H₈. Figure 3a shows the model predictions of C₁₈H₁₄
 550 where the measured mole fractions are calculated with the PICS of 3,3-bi-indene. The combination of
 551 two indenyl radicals is one of the most favorable reactions for indenyl. It consumes 21% and 76% of
 552 indenyl at 30 and 760 Torr, respectively, as shown in Fig. 7 ROP analysis at 70% indene conversion.
 553 It forms bi-indene isomers [63] which are represented by 3,3-bi-indene in the present model. 5- and
 554 11-methyl-benzofluorene are minor C₁₈H₁₄ isomers. Further reactions of C₁₈H₁₄ yield C₁₈H₁₂, which

555 can be chrysene, benzo-phenanthrene and triphenylene [10,61,63,65,109]. Model prediction shows
 556 that the quantities of chrysene and benzo-phenanthrene are comparable while that of triphenylene is
 557 smaller (chrysene 62%, benzo-phenanthrene 33%, and triphenylene 5% at ~1300 K, 760 Torr).
 558 Sensitivity analysis is performed at the temperature of 70% indene conversion at both pressures, as
 559 shown in Fig. 8. Besides the formation reactions (R88 for 3,3-bi-indene and R95 for chrysene), both
 560 species are sensitive to R99. It may be because R88 and R99 are two main branching pathways
 561 competing for the consumption of indenyl.

562

Figure 8 Sensitivity analysis performed at 70% indene conversion on the selected PAH species: (a) 3,3-bi-indene, (b) chrysene, (c) fluoranthene, (d) phenanthrene, (e) acenaphthylene and (f) naphthalene. Black and red bars indicate 30 and 760 Torr conditions, respectively.

Figure 9 ROP analysis performed for C_{13} - C_{16} species at 70% indene conversion. The blue frames highlight the larger RSRs generated by indenyl radical. Numbers beside the arrows are the contributions of this reaction step in the consumption of the precursors. Black and red colors separate 30 and 760 Torr conditions, respectively. Bold arrows indicate those reaction steps that consume > 99.5% of the precursors.

For $C_{16}H_{10}$ species, ROP analysis in Fig. 9 shows that indenyl reactions are the main formation source for fluoranthene and pyrene in all cases. The contributions from the reaction of benz-indenyl + propargyl to pyrene and fluorenyl + propargyl to fluoranthene are much smaller, and the HACA route

575 (phenanthrenyl + acetylene) is negligible. Sensitivity analysis of fluoranthene in Fig. 8c shows that not
576 only the combination of indenyl and benzyl (R63), but also the H-abstraction of phenyl-naphthalene
577 (R69) and β -scission of C-H bond of $C_{10}H_8C_6H_5$ (R67) are rate controlling reactions of $C_{16}H_{10}$ species.
578 R67 is a branching channel of this pathway. It competes with the C-C bond fission of $C_{10}H_8C_6H_5$ for
579 naphthalene and phenyl. ROP analysis shows that R67 has a conversion ratio only around 7%.

580 $C_{14}H_{10}$ is calibrated as phenanthrene in the experiments and it has similar mole fraction to $C_{16}H_{10}$,
581 shown in Fig. 3. Its dominant formation pathway is the bimolecular reaction of indenyl and
582 cyclopentadienyl (R46), which consumes 8% of indenyl, as shown in Fig. 9. Sensitivity analysis in
583 Fig. 8d also shows that R46 is the rate controlling step of phenanthrene formation pathways. The
584 combination of phenyl + phenylacetylene and the decomposition of $C_{13}H_9CH_2$ radicals (benzindenyl-
585 methyl or fluorenyl-methyl) have minor contributions. Another sensitive reaction is the decomposition
586 of phenyl-allyl radical ($A_1C_3H_4$), which is a source of cyclopentadienyl radical.

587 Two $C_{12}H_8$ species are proposed in this study, i.e., acenaphthylene and ethynyl-naphthalene
588 [40,110,111]. Both of these may be formed by the addition of acetylene on naphthyl radical, which are
589 competing HACA channels. When comparing their contributions to indenyl routes, HACA routes are
590 minor. The reaction of indenyl and propargyl (R27) forms more $C_{12}H_8$ species (> 80%). Branching
591 channels of R27 and R35 lead to the formation of acenaphthylene and vinyl-naphthalene, whose ratios
592 are shown in Fig. 10. Sensitivity analysis of acenaphthylene in Fig. 8e illustrates that the formation
593 efficiency of propargyl significantly influences its concentration.

594 $C_{10}H_8$ is the summation of naphthalene, azulene and methylene-indene, which is calibrated as
595 naphthalene in this experiments. $C_{10}H_8$ has higher mole fraction than $C_{16}H_{10}$, $C_{14}H_{10}$ and $C_{12}H_8$ but
596 less than $C_{18}H_{12}$, as shown in Fig. 3. ROP analyses in Figs. 9 and 10 indicate that the main naphthalene
597 formation pathway changes from methyl addition on indenyl to the decomposition of $C_{10}H_8C_6H_5$
598 radical. This radical is the product of indenyl and benzyl combination via R63-R66. The former
599 pathway consumes 11% of indenyl at 30 Torr, and drops to 1% at 760 Torr. In contrast, the contribution
600 of R63 increases 5 times with pressure. Sensitivity analysis of naphthalene also reflects this

601 observation. R16 is very sensitive at 30 Torr, while benzyl formation reaction is very sensitive at 760
 602 Torr.

603
 604 **Figure 10** ROP analysis performed for C₁₀-C₁₂ species at 70% indene conversion. The blue frame
 605 highlights larger RSR generated by indenyl radical. Numbers beside the arrows are the
 606 contributions of this reaction step in the consumption of the precursors. Black and red
 607 colors separate 30 and 760 Torr conditions, respectively. Bold arrows indicate those
 608 reaction steps that consume > 99.5% of the precursors.

609 In a general view of the sensitivity analysis of PAH species, shown in Fig. 8, we observe that the
 610 low-pressure limit (LPL) of R1 is always sensitive at low pressure, and R2 is sensitive at high pressure.
 611 On one hand, indenyl is mainly formed via R1 at low pressure, while on the other hand, R1 provides
 612 H atoms that enhance the formation of indanyl. It leads to small intermediates which are the source for
 613 addition reactions to PAHs. R2 has positive sensitivity for 3,3-bi-indene and chrysene, but negative
 614 for fluoranthene, phenanthrene, acenaphthylene and naphthalene. This is because H-abstraction of
 615 indene (R2) is competing with H-addition of indene (R3). The formation of latter four PAHs not only
 616 needs indenyl but also corresponding small intermediates.

617

618

619 5.1.5. Uncommon PAHs formation

620 Figure 4 shows some PAH species that are not commonly included in previous modeling studies.
621 They are normally odd C-number species that are ignored in traditional HACA mechanism but are
622 considered to be critical in this study *via* radical combination PAH pathways. $C_{17}H_{12}$ is speculated
623 to be benzo-fluorene [65], and its mole fraction increases significantly with the pressure. $m/z = 190$ is
624 $C_{15}H_{10}$, and its molecular structure is proposed to be 4*H*-cyclopenta[def]phenanthrene in literature
625 [112,113]. ROP analysis shows that its formation consumes less than 0.1% of indenyl. Since bi-indene
626 is detected in this study, indenyl-cyclopentadiene, having similar reactivity, is also detectable by the
627 same technique. It could be a candidate of $C_{14}H_{12}$ species. Other possible $C_{14}H_{12}$ isomers are methyl-
628 fluorene and methyl-benzindene. Quantitative modelling results show that the mole fractions of the
629 latter two isomers are higher than that of indenyl-cyclopentadiene. The reactions of $C_9H_8 + C_5H_5$ and
630 $C_9H_7 + C_5H_6$ are not favored to produce indenyl-cyclopentadiene, but are more likely to form fluorene
631 and benz-indene ($C_{13}H_{10}$), as shown by the ROP analysis in Fig. 9. We also observe from ROP analysis
632 that $C_9H_7 + iC_4H_3$ reaction has considerable contribution in fluorene formation. $C_{11}H_8$ is calibrated as
633 ethynyl-indene in the experiments [53,96,114]. In general, the proposed formation pathways in the
634 present model reproduce the measured mole fraction quite well at both pressures, as shown in Fig. 4.

635 $C_{10}H_{10}$ is speculated as methyl-indene in this work [53,96,114]. The model under-predicts the
636 formation of $C_{10}H_{10}$ in Fig. 4f. It could be because of the unknown methyl-indene formation pathways
637 or the under-prediction of methyl radical at temperatures around 1100 K. An important source of
638 methyl radical is the reaction of indenyl and indene. It produces benzo-fluorene while releasing a
639 methyl radicals. However, this part of the present model is analogized to the kinetics of
640 cyclopentadienyl radical, which may introduce large uncertainty to methyl prediction. Further detailed
641 calculations of this scheme at the potential energy surface of $C_{18}H_{15}$ may reveal the kinetics of benzo-
642 fluorene and methyl-indene.

643

644

645 **5.1.6. PAHs grown from other RSR radicals**

646 Generally, PAH species can be divided into different aromatic groups: monocyclic, bicyclic,
647 tricyclic, etc. Five-member-ring RSRs can be formed in every aromatic group as highlighted by the
648 blue rectangles in Figs. 7 and 9. The smallest five-member-ring RSR is cyclopentadienyl radical.
649 Indenyl radical studied in this work is a bicyclic five-member-ring RSR. With the addition of other
650 five-member-ring species, the five-member-ring RSRs could grow bigger through self-incentive
651 reaction processes. For example, indene is yielded from cyclopentadienyl radical [49,86,115] while
652 fluorene and benz-indene are yielded *via* $C_9H_7 + C_5H_6$ or $C_5H_5 + C_9H_8$ [50]. Therefore, similar
653 reactions are also possible for fluorenyl, benz-indenyl, benzo-fluorenyl and even larger five-member-
654 ring RSRs. This efficient PAH growth moiety agrees with the radical chain reaction, recommended
655 recently by Johansson et al. [59].

656 Besides the five-member-ring RSRs, the contribution of other RSRs is not so remarkable in indene
657 pyrolysis, which can be ascribed to the fuel selectivity of PAH growth pathways. Propargyl, benzyl,
658 troyl, vinyl-cyclopentadienyl, and other large RSRs with similar structures are potential contributors.
659 For example, in Figs. 9 and 10, the addition reactions of propargyl on indenyl and fluorenyl are quite
660 efficient to build larger PAHs. Detailed chemical kinetics for some of these were investigated in
661 previous studies [31,42,45,47,54,85,116-120]; however, there is a lack of knowledge about more other
662 RSRs, especially large ones, which may be comparatively as important as indenyl in PAH growth.

663

664 **5.2 Indene pyrolysis in shock tube**

665 Laskin and Liftshitz studied indene pyrolysis in a shock tube at a pressure of 3.7 atm over a
666 temperature range of 1150 – 1900 K [62]. Quantitative species measurements were provided by gas
667 chromatography (GC). We adopted this dataset to validate the present model. Comparisons between
668 experimental data and simulations are presented in Figs. 11 and 12. Note that simulated temperatures
669 were shifted by 80 K to match indene conversion [121,122] in order to compare experimental and
670 simulated branching fractions for an equivalent conversion. The present model adequately captures

671 the mole fractions of most species; only a few species, like naphthalene, methylene-indene and
672 benzene, are slightly over-predicted. Predictions by literature models are also compared in Figs. 11
673 and 12.

674

675 **Figure 11** Modeling results of indene decomposition in a shock tube; experimental data are taken
676 from [62]. Simulated results were shifted by 80 K according to the literature [121,122].
677 MPR: present model; MPO: Polimi model [81]; MYU: Yuan et al.'s model [9]; MLL:
678 Laurence Livermore model [58]; MBL: Blanquart et al.'s model [7]; MKA: Wang et al.'s
679 model [8].

680

681 **Figure 12** Predicted mole fraction profiles of the species measured in shock tube indene pyrolysis
682 [62]. Simulated results were shifted by 80 K according to the literature [121,122]. MPR:
683 present model; MPO: Polimi model [81]; MYU: Yuan et al.'s model [9]; MLL: Laurence
684 Livermore model [58]; MBL: Blanquart et al.'s model [7]; MKA: Wang et al.'s model [8].

685

686 **6. Conclusions**

687 Pyrolysis of indene was investigated in a flow reactor at 30 and 760 Torr over the temperature
688 range of 975 - 1450 K using SVUV-PIMS. A number of pyrolytic species were quantified, such as
689 free radicals, various small hydrocarbons and PAHs. Their mole fraction profiles were measured as a
690 function of reactor temperature. Based on these experimental observations, an improved kinetic model
691 was developed based on previous PAH models [7,9,10,13-15,56,57,66,77]. We adopted recent
692 theoretical progress and added some necessary reaction schemes in our model. The present model was
693 then validated against the flow reactor data from this study and datasets reported in literature [62]. By
694 performing ROP and sensitivity analysis, critical reaction pathways were identified for indene
695 pyrolysis, particularly those leading to PAH formation from indenyl radical.

696 Under the pyrolysis condition, indene is mainly consumed by unimolecular C-H bond dissociation
697 and H-abstraction reactions. Both of these pathways have comparable contribution from low to
698 atmospheric pressure. Subsequent reactions of indenyl favor the PAH channels, since indenyl is not
699 easy to decompose at the conditions of this study. The dominant PAH formation pathways in this study
700 are the bi-molecular addition reactions of indenyl radical with indene or a series of other intermediates.
701 PAH growth also has particular contribution from the reactions of other resonantly stabilized radicals
702 with five-member ring in their molecular structures, such as cyclopentadienyl, fluorenyl, benz-indenyl
703 and benzo-fluorenyl. Radical chain reactions provide huge passage for PAH growth from one RSR to
704 larger ones. Typically, the cyclical addition of acetylene on indenyl yields vinyl-indenyl or benz-
705 indenyl, while the cyclical addition of indene on indenyl yields benzo-fluorenyl and even larger RSRs,
706 although these RSRs are not detected in this study. Further PAH modeling studies should refine the
707 reaction network of other typical RSRs besides indenyl radical, which may help provide prediction of
708 not only the concentration but also the chemical and/or physical structures of PAHs and soot.

709

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Figure Captions

(Color figures in electronic version only)

Scheme 1 (a) C-H and (b) C-C bond energies of indene, calculated at 298 K. Unit: kcal/mol.

Scheme 2 Reaction scheme proposed for $C_9H_7 + C_3H_3$. Solid arrows represent elementary reaction steps. Blue dashed arrow highlights the key reaction step.

Scheme 3 Reaction scheme proposed for $C_9H_8 + C_5H_5$ and $C_9H_7 + C_5H_6$. Solid arrows represent elementary reaction steps; dashed arrows represent reactions with multiple steps.

Scheme 4 Reaction scheme proposed for $C_9H_7 + C_6H_5$. Solid arrows represent elementary reaction steps; dashed arrows represent reactions with multiple steps.

Scheme 5 Reaction schemes (a) for $C_5H_6 + C_5H_5$ calculated by Kislov et al. [86], (b) proposed here for $C_9H_8 + C_9H_7$. Solid arrows represent elementary reaction steps; broad arrows represent reactions with multiple steps.

Scheme 6 Reaction schemes (a) for $C_5H_5 + C_5H_5$, (b) proposed for $C_9H_7 + C_9H_7$. Solid arrows represent elementary reaction steps; dash arrows represent reactions with multiple steps.

Figure 1 Measured mole fraction profiles of indene (C_9H_8) and its main decomposition products in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines are predictions of the current model.

Figure 2 Mole fraction profiles of small intermediates measured in indene pyrolysis in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines are the predictions of the present model. Experimental data and simulations of species with small concentration are scaled with a common factor.

Figure 3 Mole fraction profiles of dominant (common) PAHs measured in indene pyrolysis in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines indicate the model predictions.

Figure 4 Mole fraction profiles of uncommon PAHs measured in indene pyrolysis in a flow reactor at 30 (*black squares*) and 760 (*red circles*) Torr. Shadows with the data plots represent the uncertainty of the measurements. Lines indicate the model predictions.

Figure 5 Reaction flux analysis of indene decomposition at 17.5% conversion. Arrows indicate reaction steps; the numbers indicate the conversion ratios of each step at 30 (black) and 760 torr (red).

038 **Figure 6** Sensitivity of R1 (a) and R2 (b) to the consumption of indene at 30 and 760 Torr. The dash
039 lines and dotted lines are the simulation results of indene using the rate coefficients of R1
040 and R2 multiplied or divided by a factor of three.

041 **Figure 7** Main PAH formation pathways according to the present model: (a) indenyl reactions to
042 form C₁₀-C₁₂ species, (b) indenyl reactions to form C₁₇ and C₁₈ species. The blue frame
043 highlights the larger RSR generated by indenyl radical.

044 **Figure 8** Main PAH formation pathways according to the present model from indenyl to C₁₃-C₁₆
045 species. The blue frames highlight the larger RSRs generated by indenyl radical.

046 **Figure 9** Modeling results of indene decomposition in a shock tube; experimental data taken from
047 [62]. Simulated results were shifted by 80 K according to the literature [121,122].

048 **Figure 10** Predicted mole fraction profiles of the species measured in shock tube indene pyrolysis
049 [62]. Simulated results were shifted by 80 K according to the literature [121,122].

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l052 **Supplementary Materials**

l053 SMM1. Temperature profiles measured along the flow reactor.xlsx

l054 SMM2. Experimental details.docx

l055 SMM3. Quantum calculation.docx