

Chemical kinetics of hydroxyl reactions with cyclopentadiene and indene

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Abstract

Oxidation reactions of highly unsaturated cyclic hydrocarbons are very important in combustion, competing with their participation in PAH and soot growth. One of the key oxidation pathways at combustion conditions is the reaction with hydroxyl radicals. Cyclopentadiene (C₅H₆) and indene (C₉H₈) are typical PAH precursors, which have highly unsaturated penta-ring structure. In this study, rate coefficients of the reactions of hydroxyl radical with cyclopentadiene and indene were measured behind reflected shock waves over the temperature range of 828 - 1390 K and pressure near 1 atm. Hydroxyl radicals were monitored by a narrow line-width laser absorption near 306.7 nm. The measured rate coefficients may be expressed as $k_{C_5H_6+OH} = 3.68^{+0.27}_{-0.23} \times 10^{13} e^{-(1742.5^{+75}_{-77})/T}$ and $k_{C_9H_8+OH} = 1.44^{+0.10}_{-0.14} \times 10^{13} e^{-(1497.8^{+130}_{-72})/T}$ cm³mol⁻¹s⁻¹. Our experimental results showed that the reaction of hydroxyl radicals with cyclopentadiene is about two times faster than that of indene, and the indene + OH reaction exhibited a relatively weaker temperature dependence. Chemical kinetic simulations, carried out with a detailed model, showed the sensitivity of model performance to these reactions and the potential of model improvement with our measured rate coefficients.

Keywords: Hydroxyl radical; Laser absorption; Indene; Cyclopentadiene; Shock tube; Rate coefficients.

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23 **1. Introduction**

24 Polycyclic aromatic hydrocarbons (PAHs) and soot are mutagenic and carcinogenic compounds
25 formed as a result of incomplete combustion [1,2]. Large efforts have been contributed from scientists
26 and researchers worldwide to understand the chemistry of their formation processes [3-6]. The
27 discovery of hydrogen-abstraction-C₂H₂-addition (HACA) mechanism was a pioneering work on PAH
28 and soot formation in the 1990s [7]. Later, Marinov et al. [8] and Richter et al. [9] carried out early
29 investigations on the role of radical combination reaction pathways in the formation of large PAHs
30 and soot [10-14]. Recently, Johansson et al. [15] concluded that resonantly stabilized radical chain
31 reactions may explain soot inception and growth, with cyclopentadienyl (C₅H₅), indenyl (C₉H₇), vinyl-
32 indenyl, etc., as key intermediates in this process. Therefore, their formation reactions from
33 cyclopentadiene (C₅H₆) and indene (C₉H₈) need to be studied.

34 A number of efforts have been carried out on the thermal decomposition of cyclopentadiene and
35 indene [14-42]. Szwarc [16], Burcat and Dvinyaninov [20], Roy et al. [21,22] and Kern et al. [23]
36 studied the C-H bond dissociation energy of cyclopentadiene and subsequent decomposition of
37 cyclopentadienyl radical. Spielman and Cramers [17], Cypres and Bettens [18] and Manion and Louw
38 [19] proposed the mechanism of cyclopentadiene formation from naphthalene and indene; this was
39 revealed in detail in later works [14,24-31]. Recent experimental and kinetic modeling study of
40 Vervust et al. [32] provided comprehensive speciation, model validation and kinetic analysis of
41 cyclopentadiene pyrolysis. Indene is an important transmitting platform in the aromatic growth
42 sequence [15,33,34], and it has very similar molecular structure as cyclopentadiene. It could be easily
43 formed via the reaction of cyclopentadiene and cyclopentadienyl radical [43]. Compared to
44 cyclopentadiene, chemical kinetic studies are limited for indene [34-43]. Badger and Kimber [41]
45 carried out pioneering work on indene pyrolysis, and Laskin and Lifshitz [36] measured thermal
46 decomposition products of indene behind reflected shock waves. Flash pyrolysis studies on indene
47 were carried out by Ajaz et al. [35] and Wentrup et al. [37]. Wentrup et al. [37] revealed the
48 interconversion between indene and 2-ethynyl-toluene by Roger-Brown rearrangement *via* quantum

49 chemical calculations. Indene related theoretical studies have focused on the addition reactions of
50 indenyl [37-39,43]. Most recently, Jin et al. [34,42] measured indene pyrolysis species in a flow reactor
51 at various temperatures (975 - 1450 K) and pressures (30 - 760 Torr) by synchrotron vacuum ultra-
52 violet photoionization mass spectrometry. They provided the first detailed kinetic model describing
53 the dissociation of indene and PAH growth pathways of indenyl radical.

54 The oxidation of aromatic species is also an indispensable part that needs to be understood in the
55 chemistry of PAH and soot. On one side, the oxidation of PAHs and soot breaks them down to small
56 hydrocarbons and reduces their concentrations; on the other side, oxidation process also creates
57 radicals and activates the reaction system that may promote the reactions for further PAH and soot
58 growth [44,45]. In contrast to the literature on the formation of unsaturated or aromatic hydrocarbons
59 and their further aggregation, few studies focused on their oxidative behaviors in combustion
60 conditions. Burcat et al. [46] studied the oxidation of cyclopentadiene in a shock tube. They reported
61 its ignition delay times and the concentrations of combustion intermediates and products in the
62 temperature range of 1278 - 2110 K and pressure range of 2.43 - 12.45 atm. Murakami et al. [47] also
63 monitored the oxidation of cyclopentadiene behind shock waves, and reported the O-atom and CO
64 time-history. A preliminary kinetic model was assembled to reproduce their experimental
65 measurements. Later, Butler and Glassman [48] investigated the combustion of cyclopentadiene in a
66 flow reactor near 1150 K at atmospheric pressure. Time dependent concentration profiles of major
67 species were reported for equivalence ratios of 0.6 – 100. They found the formation and dissociation
68 of cyclopentadienoxy radical (C_5H_5O) as being important in cyclopentadiene oxidation. Djokic et al.
69 [27] proposed a detailed kinetic model for cyclopentadiene oxidation, which was validated by
70 speciation data of Butler and Glassman [48] and flame speed data of Ji et al. [49]. Most recently, Wang
71 et al. [50] further developed cyclopentadiene model based on speciation of its pyrolysis and oxidation
72 by synchrotron vacuum ultra-violet photoionization mass spectrometry, and showed improved
73 prediction accuracy than previous models. Their model revealed that the reaction with hydroxyl was
74 the dominant cyclopentadiene consumption pathway in both fuel-lean and fuel-rich conditions at

75 temperatures near 1000 K. For indene, to the authors' knowledge, not a single study has been carried
76 out on its gas phase oxidation kinetics under combustion condition.

77 Certainly, reactions with hydroxyl radicals are among the most important reactions in the
78 oxidation process of cyclopentadiene and indene (R₁ and R₂). Emdee et al. [51] gave the first
79 estimation of the rate coefficient of R₁ ($3.43 \times 10^9 T^{1.18} e^{-225/T}$ cm³mol⁻¹s⁻¹) in their study of toluene
80 oxidation since the mechanism of cyclopentadiene is a subset of toluene. Zhong et al. [52]
81 recommended an expression of $3.08 \times 10^6 T^{2.0}$ cm³mol⁻¹s⁻¹ based on their quantum calculation for R₁.
82 Robinson and Linstedt [53] used a value of R₁ which was smaller by a factor of 3 compared to Emdee
83 et al. [51]. Since indene has a similar molecular structure as cyclopentadiene, previous kinetic models
84 analogized the reaction scheme of indene from cyclopentadiene [8,54-56].



87 In the current work, rate coefficients of R₁ and R₂ are measured behind shock waves at
88 temperatures of 828 - 1390 K and pressures of 0.77 - 1.30 atm. Mixture compositions are designed to
89 study the reactions under pseudo-first-order condition. Toluene mechanism of Yuan et al. [56] was
90 used to model the hydroxyl time histories. Our measurements of R₁ and R₂ are compared to previous
91 estimations and quantum calculations. Rate coefficients measured in this study are also validated in
92 the model performance to highlight the sensitivity of these reactions to the reactivity of combustion
93 systems.

94

95 **2. Experimental details**

96 **2.1 Shock tube experiment**

97 All rate coefficient measurements reported in this study were carried out in the shock tube facility
98 at King Abdullah University of Science and Technology (KAUST). The shock tube has an inner
99 diameter of 14.2 cm, driven section is 9 m long while the driver section length is flexible. Five PCB

100 (Model 113B26) piezo-electric pressure transducers are spaced over the last 1.3 m of the driven section
101 to determine the incident shock velocity. Temperature (T_5) and pressure (P_5) behind shock waves are
102 calculated using standard shock relations. Thermochemical data are taken from Ideal Gas
103 Thermochemical Database [57]. A turbo-molecular pump (Varian TV 551) was used to evacuate the
104 driven section of the shock tube to an ultimate pressure of 2×10^{-5} mbar before each experiment. Details
105 of the shock tube facility can be found in our previous studies [58,59].

106 The time-history of OH radical concentration was measured using the well-characterized $R_1(5)$
107 absorption line of the OH A–X (0,0) band near 306.69nm. A continuous wave 532nm (10 W) green
108 laser pumped a ring-dye laser (0.75 g/L Rhodamine B in ethylene glycol) to generate visible red light
109 near 613.4 nm (~ 1.0 W). The red light was frequency doubled to generate ultraviolet light near 306.7
110 nm (~ 100 mW). A common-mode-rejection scheme was used to minimize the noise from laser
111 intensity fluctuations [59]. The mole fraction of hydroxyl radical (X_{OH}) was calculated by Beer–
112 Lambert law, $I/I_0 = e^{-k_\nu X_{OH} P_5 L}$, where I and I_0 are the transmitted and incident laser intensities,
113 respectively; k_ν is the absorption coefficient calculated following the work of Herbon [60], P_5 is the
114 pressure after reflected shock (atm) and L is the optical path length (14.2 cm). All experimental data
115 were recorded at 2.5 MHz sampling rate using a high-resolution (14 bit) data acquisition system.

116 Gas mixtures were prepared using argon (99.999%), 70% tert-butyl-hydroperoxide (TBHP)
117 aqueous solution and dicyclopentadiene (99%) or indene (98%). TBHP is a well-known thermal
118 precursor of OH radicals [61]. Dicyclopentadiene was sufficiently depolymerized at 200 °C in a closed
119 container before its expansion into a pre-evacuated mixing tank. This process should result in a
120 conversion of more than 99% of dicyclopentadiene to cyclopentadiene, according to previous works
121 [20,49,62]. High-purity helium (99.99%) was used as the driver gas. All gases were provided by AH
122 Gases and the other chemicals were obtained from Sigma-Aldrich. Mixture compositions were chosen
123 to have hydroxyl decay follow pseudo-first-order kinetics; 250 ppm cyclopentadiene / ~ 28 ppm TBHP
124 and 400 ppm indene / ~ 27 ppm TBHP in argon. Mixing tank and shock tube were heated to 323 K to
125 avoid condensation. Detailed procedure for the depolymerization of dicyclopentadiene, gas mixture

126 preparation and the impact of the impurities in the indene sample on the rate coefficient determination
127 are provided in the Supplementary Material.

128 **2.2 Jet-stirred reactor experiment**

129 Indene oxidation we investigated in a jet-stirred reactor (JSR) coupled to a gas chromatograph
130 (GC) at KAUST. Details of this facility may be found in a previous publication [63]. The composition
131 of the inlet indene mixture was 0.10% C₉H₈ / 3.14% O₂ / 96.76% Ar ($\phi = 0.35$), and the residence time
132 was kept at 2.0 s at various temperatures. Indene consumption profile was recorded by GC as a function
133 of reaction temperature.

134 **3. Rate coefficient measurements**

135 **3.1 Kinetics of cyclopentadiene and hydroxyl radical**

136 Experiments were carried out behind reflected shock waves over the temperature range of 828 -
137 1390 K and pressure range of 0.77 - 1.27 atm. Detailed conditions of every shock are listed in Table
138 1. Sensitivity analysis of hydroxyl time-history by the model of Yuan et al. [56] (MYU), shown in Fig.
139 1, indicates that the reaction of hydroxyl and cyclopentadiene (R₁) is dominant. TBHP dissociates very
140 quickly which determines the initial hydroxyl concentration in the reaction system; other reactions like
141 the recombination of OH with C₅H₅ and the decomposition of C₅H₄OH have negligible influence on
142 the hydroxyl time-history.

143 Figure 2 presents a typical hydroxyl time-history in its high temperature reaction with
144 cyclopentadiene. Time-zero indicates the arrival of the reflected shock wave. TBHP completely
145 dissociates to hydroxyl radical in less than 3 μ s. Hydroxyl radicals then start to be consumed by
146 reaction with cyclopentadiene, obeying first-order kinetics, as can be seen in the inset of Fig. 2. The
147 rate coefficient of R₁ can be evaluated by the slope of hydroxyl concentration in logarithmic scale.
148 Alternatively, the rate coefficients are extracted by using the kinetic model of Yuan et al. [56] (MYU),
149 where TBHP sub-mechanism was added from Pang et al. [64]. Best fit of the hydroxyl time-history
150 was achieved by iteratively changing the rate coefficient of R₁. Numerical simulations of shock tube
151 was performed with OpenSMOKE++ [65] using the constrains of constant UV. As shown in Fig. 2, a

152 small perturbation of rate coefficient k_1 ($\pm 25\%$) could lead to a significant change of OH profile, which
153 illustrates the sensitivity of rate coefficient evaluation. Measured rate coefficients (k_1) are listed in
154 Table 1, and are compared with literature estimations and theoretical calculations in Fig. 3.

155 Some previous models [34,54,67] used the rate coefficients of R₁ calculated by Zhong and
156 Bozzelli [52]. According to the calculation of Zhong and Bozzelli [52], the reaction between hydroxyl
157 and cyclopentadiene has three product channels, (i) abstraction reaction to H₂O + C₅H₅, (ii) addition
158 reaction followed by ring open process to C₅H₅OH, and (iii) well-skip decomposition reaction to C₂H₂
159 + C₃H₄OH. In Fig. 3, calculated rate coefficients of Zhong and Bozzelli [52] are plotted, which are
160 higher than our measurements, particularly at temperatures lower than 1100 K. Early models [8,55,68]
161 applied the estimation used in the model of Emdee et al. [51] (MEM). Robison and Lindstedt [53]
162 reduced the estimation of Emdee et al. [51] by a factor of three in their model, and their values are
163 close to our measurements. The highest rate coefficient values proposed by MPO [69] overestimate
164 our measured rates by about one order of magnitude. Our measured rate coefficients of R₁ exhibit
165 Arrhenius behavior over the temperature range of this study. Black solid line (Fig. 3) shows the best
166 fit of our high-temperature experimental data by the expression $3.68_{-0.23}^{+0.27} \times 10^{13} e^{-(1742.5 \pm 75)/T}$
167 cm³mol⁻¹s⁻¹. Grosjean and Williams [66] reported the rate coefficients of R₁ at low temperatures which
168 exhibit negative temperature coefficient, likely due to the dominance of OH addition channel at low
169 temperatures. The experimental data at low and high temperature ranges are fitted by two separate
170 Arrhenius expressions, as shown by solid red and black lines in Fig. 3; the sum of these (cyan dash
171 line in Fig. 3) reproduces the data across the entire temperature range. Hydroxyl addition reaction can
172 be very important at low temperature, while abstraction reaction dominates at higher temperatures.

173 **3.2 Kinetics of indene and hydroxyl radical**

174 Rate coefficients of indene + OH were measured behind reflected shock waves over the
175 temperature range of 859 - 1352 K and pressure range of 1.12 - 1.30 atm. Detailed conditions of every
176 experiment are listed in Table 2. We performed sensitivity analysis of hydroxyl time-history by MYU
177 model [56] to figure out the reactions that have significant impact on its concentration. As shown in

178 Fig. 4, the reaction of hydroxyl and indene (R₂) is dominant over the time frame of our experiment.
179 Due to the incomplete indene oxidation reaction scheme in MYU and other literature models, we do
180 not observe any sensitivity from hydroxyl and indenyl reactions, like the recombination of hydroxyl
181 with cyclopentadienyl (see Fig. 1).

182 Figure 5 presents a typical hydroxyl time-history during its high temperature reaction with indene.
183 TBHP completely dissociates to hydroxyl radical in less than 3 μs behind the reflected shock wave.
184 The concentration of hydroxyl radical obeys first-order kinetics, as shown in the inset of Fig. 5. The
185 rate coefficient of R₂ can be evaluated by the slope of hydroxyl concentration in logarithmic scale.
186 Similar to cyclopentadiene, the rate coefficients of R₂ are extracted by using the MYU model [56]. As
187 shown in Fig. 5, a small perturbation of the rate coefficient k_2 (±25%) results in a significant change
188 of OH profile, which illustrates the accuracy of the rate coefficient evaluation. All k_2 values measured
189 in this work are listed in Table 2, and are compared with literature estimations in Fig. 6.

190 Our measurements of k_2 show a small positive temperature dependence, with a value of 3.28×10^{12}
191 $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ near 1000 K. Lindstedt et al. (MLI) [73] estimated k_2 as a temperature-independent value,
192 $5.0 \times 10^{10} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$, which is almost two orders of magnitude smaller than our measurements. Models
193 of Yuan et al. (MYU) [56] and Blanquart et al. (MBL) [54] use the same estimation for k_2 . It also has
194 a positive temperature dependence, but one order of magnitude smaller than our experimental data. On
195 the other hand, models from Mati et al. (MMA) [72] and Polimi (MPO) [69] overestimate the rate of
196 R₂ by almost one order of magnitude. As shown in Fig. 6, model of Lawrence Livermore National
197 Laboratory (MLL) [8] has the highest rate coefficients, which includes not only the abstraction channel
198 but also a direct decomposition channel to CO, ethylene and phenyl. Black solid line in Fig. 6
199 represents the best fit of our measurements of k_2 by a standard Arrhenius expression,
200 $1.44_{-0.14}^{+0.10} \times 10^{13} e^{-(1497.8_{-72}^{+130})/T} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Kwok et al. [70] and Baulch et al. [71] reported the rate
201 coefficient of k_2 near 300 K. We changed the A-factor of the low-temperature expression of OH +
202 C₅H₆ to get the best-fit to the low-temperature data of OH + C₉H₈, as shown by the red solid line in

203 Fig. 6. The sum of black and red solid lines is considered a reasonable expression for k_2 over the entire
204 temperature range (300 – 1400 K).

205 **3.3 Comparison on the kinetics of cyclopentadiene and indene**

206 Measured high-temperature rate coefficients of R₁ and R₂ are compared in Fig. 7. Cyclopentadiene
207 + OH (k_1) is about two times of indene + OH (k_2) in the temperature of 900 - 1300 K, while k_2 shows
208 a slightly smaller temperature dependence than k_1 . Theoretical calculation of the reaction between
209 propene and OH by Zádor et al. [74] showed that H-abstraction from allylic C-H site has a contribution
210 of more than 80% at high temperatures. Previous studies on diolefins (butadiene [75] and pentadiene
211 [76]) also indicated that OH-addition to the double bonds is negligible compared to the contribution
212 of H-abstraction at high temperatures. Both cyclopentadiene and indene have a five-member ring with
213 C=C bonds in their penta-ring, and have only two allylic H-atoms for abstraction reactions. The allylic
214 C-H bond energy for cyclopentadiene is 83.9 kcal/mol [77] and that of indene is 81.2 kcal/mol [78] or
215 79.1 kcal/mol [34]. Although the difference of C-H bond energy between cyclopentadiene and indene
216 is ~ 2.7 – 4.8 kcal/mol, the activation energy of the two reactions only differs by ~ 0.5 kcal/mol over
217 the range of temperatures investigated here, as shown by the fits to the measured data (Fig. 7). In the
218 absence of ab-initio potential energy calculations, we may speculate that the higher rate of reaction of
219 cyclopentadiene + OH compared to indene + OH is likely due to the difference of entropic changes in
220 the two reactions, reflecting in the pre-exponential factor of the Arrhenius expression. One of the key
221 parameters in the pre-exponent is the reaction-path symmetry factor (σ), which is defined as the ratio
222 of the rotational symmetry of the reactants to that of the transition state [79]. Symmetry numbers of
223 cyclopentadiene and indene are 2 and 1 (calculated by the method in [79]), respectively, whilst those
224 of the transition states of R₁ and R₂ are 1. Therefore, $\sigma_{R1} = 2\sigma_{R2}$, and k_1 would be about two times of
225 k_2 (see Fig. 7).

226 In order to compare the measured rates with other diolefins, in Fig. 7, we have also plotted the
227 rate coefficients of OH + 1,3-pentadiene (1,3-C₅H₈, R₃) and OH + 1,4-pentadiene (1,4-C₅H₈, R₄) [76].
228 The allylic C-H bond energies of 1,3- and 1,4-pentadiene are 83.3 kcal/mol [80] and 76.6 kcal/mol

229 [81], respectively. With very similar C-H allylic bond energies of cyclopentadiene and 1,3-pentadiene,
230 the increased rate of R₃ is largely due to the presence of 3 allylic H atoms in 1,3-pentadiene vs only
231 two allylic H atoms in cyclopentadiene. We may observe in Fig. 7 that k_3 is around 1.5 times of k_1 . As
232 for 1,4-pentadiene + OH, Khaled et al. [76] described that the ease of H abstraction from the bis-allylic
233 C-H sites is the result of super-resonance stabilization of the incipient radical, which ultimately leads
234 to higher reactivity.

235 **3.4 Uncertainty analysis**

236 Detailed uncertainty analysis was performed using root-sum-squared method to estimate the errors
237 in the measured rate constants at a specific condition [59]. The sources of errors considered here
238 include: pressure ($\pm 0.7\%$), temperature ($\pm 1.0\%$), OH absorption cross section ($\pm 5\%$, including
239 wavemeter reading ($\pm 0.002 \text{ cm}^{-1}$)), experimental profile fitting ($\pm 9\%$, including locating time-zero
240 ($\pm 0.5 \mu\text{s}$)), mixture composition ($\pm 4\%$), and mechanism uncertainty ($\pm 11\%$). The mechanism
241 uncertainty is calculated by the root-sum-squared value of rate constant errors weighted by their
242 respective sensitivity coefficients (20 most sensitive reactions besides the measured reaction at 1000
243 K, 1.1 atm). Therefore, an overall uncertainty is calculated to be $\pm 15\%$ in the temperature range of 828
244 - 1390 K and pressure near 1 atm.

245

246 **4. Sensitivity of hydroxyl reactions in model performance**

247 Oxidation of cyclopentadiene and indene in ideal reactors, such as flow reactor (FR) and jet-stirred
248 reactor (JSR), may be used to test the sensitivity of the rate coefficients measured in this study on the
249 model performance. Numerical simulations of FR and JSR were performed with OpenSMOKE++ [65].

250 Figure 8 presents the mole fractions of cyclopentadiene oxidation species as a function of
251 residence time along the FR [48]. The initial fuel composition is 2243 ppm at an equivalence ratio ϕ
252 of 1.03, and the initial temperature and pressure are 1198 K and 1.0 atm. We selected two typical
253 models to simulate the oxidation of cyclopentadiene: one is MLL [8], because it adopted the

254 calculation of Zhong and Bozzelli [52] for R_1 which is very close to the experimental measurements
255 in this study; the second model is MPO [27], its sub-mechanism of cyclopentadiene was validated by
256 the experimental data of Butler and Glassman [48], which however uses the rate coefficients for R_1
257 very different from the values measured in this study, as shown in Fig. 3. We replaced R_1 in MPO by
258 our measurements, and its simulation results are labelled as MPO* in Fig. 8. The consumption of
259 cyclopentadiene by oxidative reactions significantly slows down, as shown in Fig. 8a. The formation
260 of naphthalene, indene, benzene, butadiene, and vinylacetylene are smaller, whilst propenal, allene,
261 propyne and acetylene are larger. In general, MPO* provides improved performance compared to
262 MPO; the predicted profiles by MPO* have a better agreement with the experimental data, particularly
263 at residence times larger than 50 ms.

264 Figure 9 presents the speciation of cyclopentadiene oxidation in a JSR at atmospheric pressure,
265 equivalence ratio of 0.5, and initial cyclopentadiene mole fraction of 1% [50]. Wang et al. [50]
266 optimized a kinetic model to reproduce their measured data; simulation results of this model are
267 labelled as MWH in Fig. 9. We replaced R_1 in MWH by the measured rate coefficient in this study,
268 and labelled the modified model as MWH*. In Fig. 9a, the prediction by MWH* has a comparably
269 slower consumption rate of cyclopentadiene than MWH, but agrees better with the curvature of
270 experimental data. Significant changes may be observed for the prediction of intermediate species in
271 Fig. 9, which reveals the sensitivity of R_1 in the cyclopentadiene reacting system. The original model
272 (MWH) performs better for some intermediates as it was optimized to reproduce the experimental data.

273 MLL adopted the calculation of Zhong and Bozzelli [52] for R_1 ; however, it did not show good
274 predictions for the intermediates in Figs. 8 and 9. Its consumption of cyclopentadiene is slower than
275 MPO* but faster than MWH*, when similar rate coefficients of R_1 was used in both models (See Fig.
276 3). This phenomenon indicates that other cyclopentadiene reactions may also have considerable
277 sensitivity in its oxidation process, like C-H dissociation or H-abstraction by H-atom, which need
278 further optimization after the calibration of R_1 rate coefficients by our measurements (see
279 Supplementary Material for sensitivity analysis).

280 Figure 10 shows the consumption of indene measured by a gas chromatograph with a flame
281 ionization detector (GC-FID) in the JSR oxidation experiment of this study. Here, 0.1% indene was
282 diluted in oxygen and argon ($\phi = 0.35$) and the experiments were carried out at atmospheric pressure.
283 The consumption profile of indene mole fraction was measured over a temperature range of 750 - 985
284 K, which was repeated several times at each temperature. Popular PAH models, such as MLL, MBL
285 [54] and MYU [56], are adopted to simulate indene oxidation. Figure 10 shows that none of these
286 models captures the consumption of indene; only MBL has a reasonable performance. As shown in
287 Fig. 6, none of these models used the rate coefficients of R_2 close to our measured values. Recently,
288 Jin et al. [34] published an indene model (MJI) with many modifications to the indene and indenyl
289 related decomposition and aromatic growth pathways, and validated their model with the help of
290 indene pyrolysis data from their work and literatures. Here, MJI was used in the simulation of indene
291 JSR oxidation. Rate coefficients of R_2 in MJI was updated to our measurements (updated model is
292 named as MJI*). As shown in Fig. 10, the predictions of MJI* show the best agreement with
293 experimental data among all models. The sensitivity of R_2 to the oxidation process of indene can be
294 observed from the deviation of the modelling results of MJI and MJI*. Similar to the oxidation of
295 cyclopentadiene, other indene reactions may also need to be optimized to predict its oxidation
296 chemistry, such as C-H dissociation or H-abstraction by H-atom.

297

298 **5. Conclusions**

299 In this study, the rate coefficients of the reactions of hydroxyl radical with cyclopentadiene and
300 indene were measured behind reflected shock waves over the temperature range of 828 - 1390 K and
301 pressure near 1.0 atm. Our experimental results indicate that reactions of hydroxyl radical with
302 cyclopentadiene and indene have very similar rate coefficients, where the reaction of indene shows a
303 relatively weaker temperature dependence. H-abstraction channels play dominant role in the reaction
304 of hydroxyl radical with cyclopentadiene and indene at the studied temperature range with the
305 abstraction at the allylic site being the primary pathway. Hydroxyl addition to the double bond of

306 unsaturated penta-ring has a much smaller contribution at high temperatures. Reaction-path symmetry
307 becomes an important parameter among similar molecular structures, which impacts the pre-
308 exponential factor of the rate coefficient expression. Model performance of the currently measured
309 rate coefficients reveals the sensitivity of the reactions of hydroxyl radical with cyclopentadiene and
310 indene under combustion condition. Our measurements of the rate coefficients of hydroxyl radical
311 with cyclopentadiene and indene will contribute to the further improvement of PAH and soot kinetic
312 models.

313

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318

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505 **Figure Captions**

506 *(Color figures in electronic version only)*

507 **Figure 1** Typical OH sensitivity analysis for a mixture of 250 ppm cyclopentadiene with 28 ppm
508 TBHP in argon at $P_5 = 1.05$ atm and $T_5 = 1127$ K. OH sensitivity is calculated as $S =$
509 $(\partial X_{OH}/\partial k_i) \times (k_i/X_{OH})$.

510 **Figure 2** Typical OH time-history measured behind reflected shock wave, 250 ppm cyclopentadiene
511 with 28 ppm TBHP in argon at $P_5 = 1.05$ atm and $T_5 = 1127$ K. Best-fit kinetic simulation
512 gave $k_1 = 7.92 \times 10^{12}$ cm³mol⁻¹s⁻¹. Simulation results of 25% perturbations on k_1 indicate the
513 sensitivity of OH profile to the target reaction.

514 **Figure 3** Comparison of the data measured in this study for $C_5H_6 + OH \rightarrow$ products with literature
515 data. Black and red solid lines are the best fits for high and low temperature data. Cyan
516 dash line represents the fit of all experimental data. References: Grosjean and Williams
517 [66], Robinson and Lindstedt [53], Zhong and Bozzelli [52]; MEM: model of Emdee et al.
518 [51], MPO: model of Politecnico di Milano [27].

519 **Figure 4** Typical OH sensitivity analysis for a mixture of 400 ppm indene with 27 ppm TBHP in
520 argon at $P_5 = 1.15$ atm and $T_5 = 1202$ K. OH sensitivity is calculated as $S =$
521 $(\partial X_{OH}/\partial k_i) \times (k_i/X_{OH})$.

522 **Figure 5** Typical OH time-history measured behind reflected shock wave, 400 ppm indene with 27
523 ppm TBHP in argon at $P_5 = 1.17$ atm and $T_5 = 1066$ K. Best-fit kinetic simulation resulted
524 in $k_2 = 3.64 \times 10^{12}$ cm³mol⁻¹s⁻¹. Simulation results of 25% perturbations on k_2 indicate the
525 sensitivity of OH concentration to the target reaction.

526 **Figure 6** Comparison of the data measured in this study for $C_9H_8 + OH \rightarrow$ products with literature
527 data. Black and red solid lines are the best fits for high and low temperature data. Cyan
528 dash line represents the fit of all experimental data. References: Kwok et al. [70], Baulch
529 et al. [71]; MMA: model of Mati et al. [72], MLI: model of Lindstedt et al. [73], MLL:
530 model of Lawrence Livermore National Laboratory [8], MPO [27], MBL: model of
531 Blanquart et al. [54].

532 **Figure 7** Comparison of the rate coefficients of hydroxyl reaction with cyclopentadiene, indene,
533 trans-/cis-1,3- and 1,4-pentadiene [76]. Lines are the best fit of experimental data by
534 Arrhenius expression.

535 **Figure 8** Model predictions of the oxidation of cyclopentadiene in a flow reactor [48]. MLL: model
536 of Lawrence Livermore National Laboratory [8], MPO: model of Polimi [69], MPO*:
537 replaced R_1 in MPO by our measured rate coefficient.

538 **Figure 9** Model predictions of the oxidation of cyclopentadiene in a JSR reactor [50], MLL: model
539 of Lawrence Livermore National Laboratory [8], MWH: model of Wang et al. [50], MWH*:
540 replaced R_1 in MWH by our measured rate coefficients.

541 **Figure 10** Model predictions of indene oxidation in a JSR at atmospheric pressure, 0.10% C_9H_8 / 3.14%
542 O_2 / 96.76% Ar ($\phi = 0.35$). MJJ* indicates the model with updated rate coefficients of R_2
543 in MJJ.

544

545 **Supplementary Materials**

546 SMM1 Supporting information.docx