

1 Electronic Supplementary Information for " An experimental study
2 of indene pyrolysis with synchrotron vacuum ultraviolet
3 photoionization mass spectrometry "

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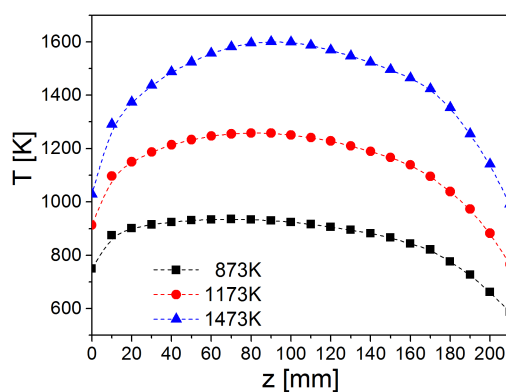
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13 1. Experimental details

14 1.1 Temperature profiles

15 Temperature of the flow reactor is controlled by W-Re thermocouple placed at the outside wall
16 of the reactor. Thus, it is important to calibrate the temperature discrepancy between the control point
17 and the reaction zone. Temperature profiles in the reaction zone are measured by an S-type
18 thermocouple, as described in the previous study ¹. As shown in Fig. S1, values along the heating zone
19 of the flow reactor are measured, where quartz nozzle is located at $z = 0$ mm. Temperature profiles are
20 also used as the input parameters in the modeling work ². Temperature profiles at the specific reactor
21 temperature can be calibrated from the interpolation of measured values.

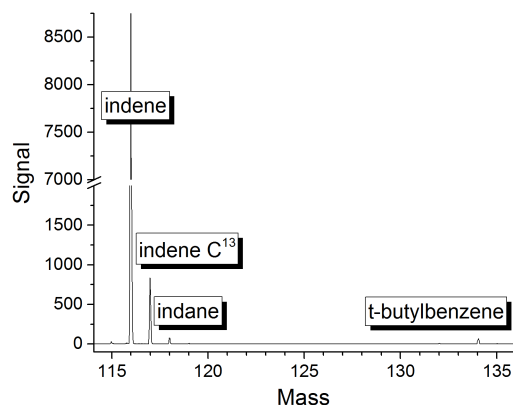


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23 **Figure S1** Temperature profiles measured along the flow reactor at three different reactor
24 temperatures. Symbols indicates the values measured by an S-type thermocouple at the
25 specific reactor temperature.

26 1.2 Purity of indene

27 The purity of indene used in this study is specified to be $\geq 97\%$ (supplier: Alfa Aesar). The
28 influence of fuel impurity on the study of kinetics should be analyzed before interpreting our
29 experimental observations. Figure S2 presents the mass spectrum of indene sample by VUV soft
30 photoionization. The highest mass peak is indene (m/z 116), and the small one (m/z 117) is its C^{13}
31 isotopic peak. Very small peaks at m/z 118 and 134 are the impurities of indene sample, probably
32 indane and t-butylbenzene. Their quantities are around 0.53% and 0.72% in the total (100%) sample.
33 Such low level of impurity ($\sim 1.25\%$) is considered to be of negligible impact on the main conclusions
34 of this experimental study.

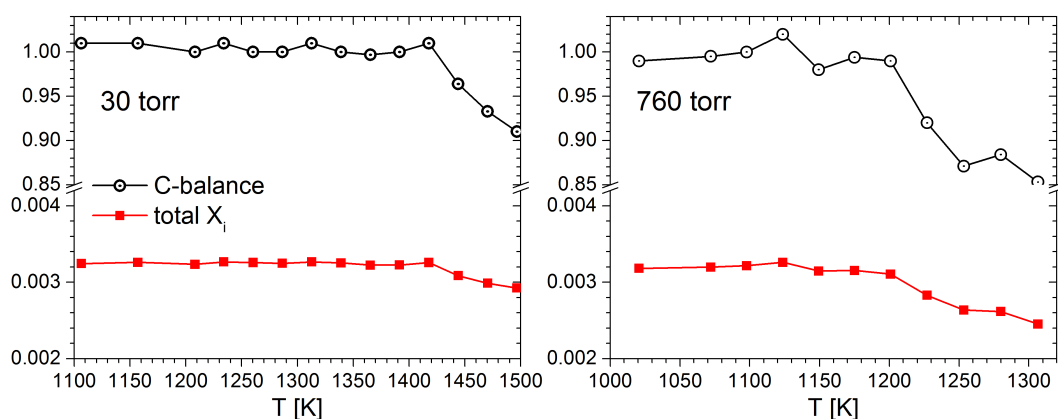


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36 **Figure S2** Mass spectrum of the impurities in fuel sample.

37 **1.3 Carbon balance**

38 Mass loss would be a considerable problem in the pyrolysis of indene, although we have
 39 performed our experiments in conditions with very low soot emissions. A check on the balance of
 40 mole fraction and carbon flux can help confirm the accuracy of our quantitative measurement. Total
 41 mole fraction is obtained by summing the contribution from all measured hydrocarbon species (X_{total}
 42 ideally equals to $1 - X_{\text{Ar}} = 0.0032$), and carbon balance is expressed as the sum of carbon in all measured
 43 species divided by the inlet carbon flux of indene. Fig. S3 presents these balances over a range of
 44 temperatures at 30 and 760 torr. These results reveal very good conservation in the measurements. A
 45 carbon loss of less than 15% is very good for such a sooty reactant in pyrolytic process.



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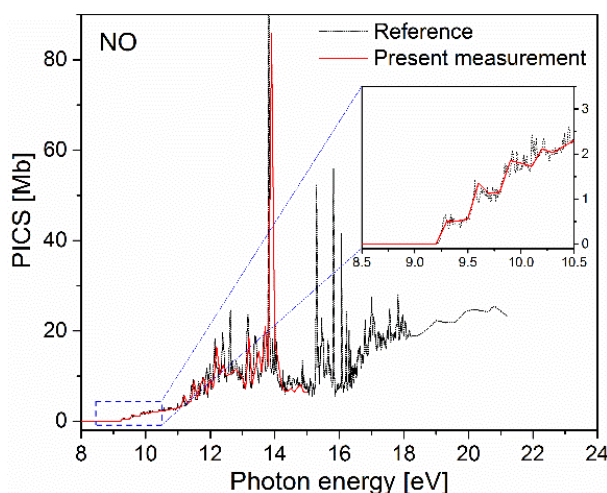
47 **Figure S3** The balance of mole fraction and carbon flux in experiments at 30 and 760 Torr.

48 **2. Photoionization cross-section (PICS)**

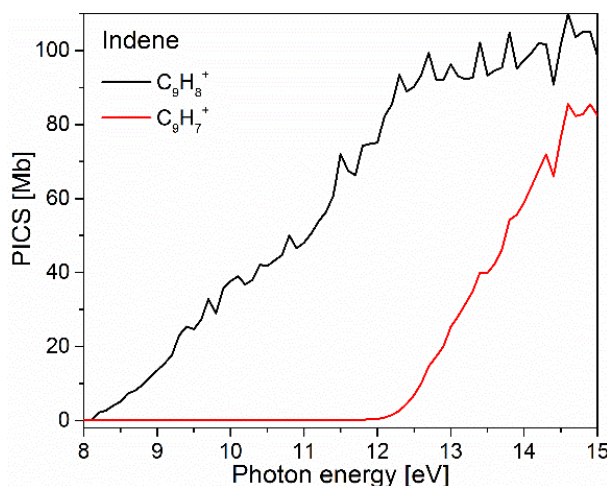
49 **2.1 Calibration of PICS**

50 PICS of the reported species are referred to three sources: 1) direct calibration, like indene; 2)
 51 literature; 3) estimation *via* similar molecules. Nitric oxide (NO) is adopted as the reference species
 52 for the calibration of indene PICS. NO has many measurements in the literature, which provide reliable
 53 PICS. The data reported in the work of Watanabe et al. ³ is taken as a reference. Figure S4 presents
 54 perfect agreement between this measurement and the literature data, and verifies the accuracy of PICS
 55 measurement by this method. The PICS of indene can be calculated by the expression below (Eq. S1),
 56 in which S is the mass signal, X is the mole fraction, σ is the cross-section, and D is the mass
 57 discrimination factor ⁴. The PICS of indene and 3-methyl-indene are presented in Figs. S5 and S6. The
 58 measurement shows that fragmentation of indene occurs when the photon energy is higher than 12.3
 59 eV, producing a $C_9H_7^+$ ion.

60
$$\sigma_{indene} = \sigma_{NO} \times \frac{S_{indene}}{S_{NO}} \times \frac{X_{NO}D_{NO}}{X_{indene}D_{indene}} \quad \text{Eq. S1}$$

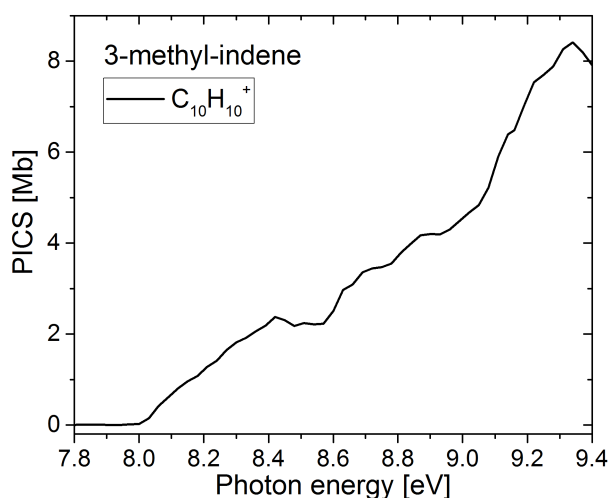


61
 62 **Figure S4** PICS of NO; comparison between this work and reference data ³.



63

64 **Figure S5** PICS of indene. The black line indicates the cross section of $C_9H_8^+$ ion, and red line
 65 indicates that of $C_9H_7^+$ ion, which is a fragment of $C_9H_8^+$.



66

67 **Figure S6** PICS of 3-methyl-indene.

68 2.2 References of PICS

69 **Table S1** below provides the PICS references adopted in the calculation of the species reported
 70 in this work. The mass, name, structure and abbreviation of these species are provided, as well as the
 71 reference literature of their cross-sections.

72 **Table S1** PICS references of reported species

Mass	Abbreviation	Name ^c	Reference
26	C ₂ H ₂	acetylene	Cool et al. ^{a,5}
39	C ₃ H ₃	propargyl	Savee et al. ^{a,6}
40	aC ₃ H ₄	allene	Yang et al. ^{a,7}
40	aC ₃ H ₄	propyne	Cool et al. ^{a,5}
50	C ₄ H ₂	butadiyne	Cool et al. ^{a,5}
52	C ₄ H ₄	vinyl-acetylene	Cool et al. ^{a,5}
65	C ₅ H ₅	cyclopentadienyl	Hansen et al. ^{a,8}
66	C ₅ H ₆	cyclopentadiene	Hansen et al. ^{a,8}
78	C ₆ H ₆	benzene	Cool et al. ^{a,5}
92	C ₇ H ₈	toluene	Zhou et al. ^{a,9}
102	C ₈ H ₆	phenylacetylene	Zhou et al. ^{a,9}
116	C ₉ H ₈	indene	pw. ^b
130	C ₉ H ₇ CH ₃	3-methyl-indene	pw. ^b
202	C ₁₆ H ₁₀	pyrene	Johansson et al. ¹⁰
228	C ₁₈ H ₁₂	chrysene	Johansson et al. ¹⁰

73 *a.* Refer to Photoionization Cross Section Database (Version 2.0)¹¹ for the estimated PICS.

74 *b.* Measured in this work.

75 *c.* Calibrated as this structure in mole fraction calculation.

76 References

- 77 1 Z. Zhou, X. Du, J. Yang, Y. Wang, C. Li, S. Wei, L. Du, Y. Li, F. Qi and Q. Wang, *J. Synchrot. Radiat.*,
78 2016, **23**, 1035-1045.
- 79 2 Y. Zhang, J. Cai, L. Zhao, J. Yang, H. Jin, Z. Cheng, Y. Li, L. Zhang and F. Qi, *Combust. Flame*, 2012,
80 **159**, 905-917.
- 81 3 K. Watanabe, Matsunaga and H. Sakai, *Appl. Opt.*, 1967, **6**, 391-396.
- 82 4 T. A. Cool, K. Nakajima, C. A. Taatjes, A. McIlroy, P. R. Westmoreland, M. E. Law and A. Morel,
83 *Proc. Combust. Inst.*, 2005, **30**, 1681-1688.
- 84 5 T. A. Cool, J. Wang, K. Nakajima, C. A. Taatjes and A. McIlroy, *Int. J. Mass Spectrom.*, 2005, **247**,
85 18-27.
- 86 6 J. D. Savee, S. Soorkia, O. Welz, T. M. Selby, C. A. Taatjes and D. L. Osborn, *J. Chem. Phys.*, 2012,
87 **136**, 134307.
- 88 7 B. Yang, J. Wang, T. A. Cool, N. Hansen, S. Skeen and D. L. Osborn, *Int. J. Mass Spectrom.*, 2012,
89 **309**, 118-128.
- 90 8 N. Hansen, S. J. Klippenstein, J. A. Miller, J. Wang, T. A. Cool, M. E. Law, P. R. Westmoreland, T.
91 Kasper and K. Kohse-Höinghaus, *J. Phys. Chem. A*, 2006, **110**, 4376-4388.
- 92 9 Z. Y. Zhou, M. F. Xie, Z. D. Wang and F. Qi, *Rapid Commun. Mass Spectrom.*, 2009, **23**, 3994-4002.
- 93 10 K. O. Johansson, M. F. Campbell, P. Elvati, P. E. Schrader, J. Zádor, N. K. Richards-Henderson, K. R.
94 Wilson, A. Violi and H. A. Michelsen, *J. Phys. Chem. A*, 2017, **121**, 4447-4454.
- 95 11 Photonization Cross Section Database (Version 2.0), <http://flame.nsrl.ustc.edu.cn/en/database.htm>,
96 National Synchrotron Radiation Laboratory, Hefei, China, 2017.
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