



## 9 S1. Identification of Oxidation Products

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11 To facilitate compound identification and differential analysis, Thermo Scientific Compound  
12 Discoverer 3.2 software was employed. Several databases, including HMDB, KEGG, BioCyc, and  
13 mzCloud, were utilized for compound identification, considering a ppm error window of 5 ppm  
14 for enhanced accuracy. Data interpretation included the determination of peak areas, putative  
15 compound identification, and the generation of comparative ratios to evaluate differences between  
16 samples. To ensure the accuracy of the comparative analysis, a filter blank was used for  
17 normalization and reference purposes for the comparative ratios. This comprehensive  
18 methodology enabled the systematic analysis of OPAHs and other compounds in the samples,  
19 providing valuable insights into their presence and potential implications. The results of this  
20 experiment are semi-quantitative without authentication with standards as the main focus was to  
21 identify the reactions products of both pyrene and 1-methylpyrene.

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23 A comprehensive set of compounds was generated using specialized software, drawing from three  
24 distinct spectral libraries. To focus exclusively on OPAHs resulting from oxidation processes, a  
25 systematic filtering procedure was executed, comprising the following steps:

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27 1. Ratio-Based Selection: In order to isolate OPAHs generated during oxidation, compounds  
28 exhibiting a two-order-of-magnitude difference in comparative ratios (viz., sample/blank) between  
29 0 and 300 minutes of ozone exposure were included in the analysis represent by a black line in  
30 figure S1 and S2. This step aimed to identify compounds whose concentrations underwent  
31 significant alterations over the exposure period.

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33 2. Chemical Formula Criterion: To further refine the selection, compounds not conforming to the  
34  $C_xH_yO_z$  chemical formula were systematically excluded. This criterion ensured that only  
35 compounds sharing the essential compositional attributes of OPAHs were retained for further  
36 consideration.

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38 3. Elimination of Duplicates: To ensure data consistency and accuracy, any duplicate compounds  
39 identified across the three spectral libraries were removed. This step aimed to prevent redundant  
40 or overlapping data entries, enhancing the overall quality of the dataset.

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42 4. Assignment of Source: Each remaining compound was scrutinized to ascertain its origin as a  
43 product of pyrene, 1-methylpyrene, or both. This assignment was achieved by evaluating the  
44 change in ratio between compounds subjected to 0 and 300 minutes of ozone exposure, providing  
45 insights into the specific precursor compounds involved in OPAH formation shown in Figure S1  
46 and S2.

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48 By following this rigorous filtering protocol, the dataset was refined to exclusively encompass  
49 OPAHs generated through oxidation processes, providing a focused foundation for subsequent  
50 analysis and interpretation.

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58 Figure S2. Overall signal (in arbitrary units) of OPAHs produced by pyrene at 0 (blue) and  
59 300mins (orange) exposure

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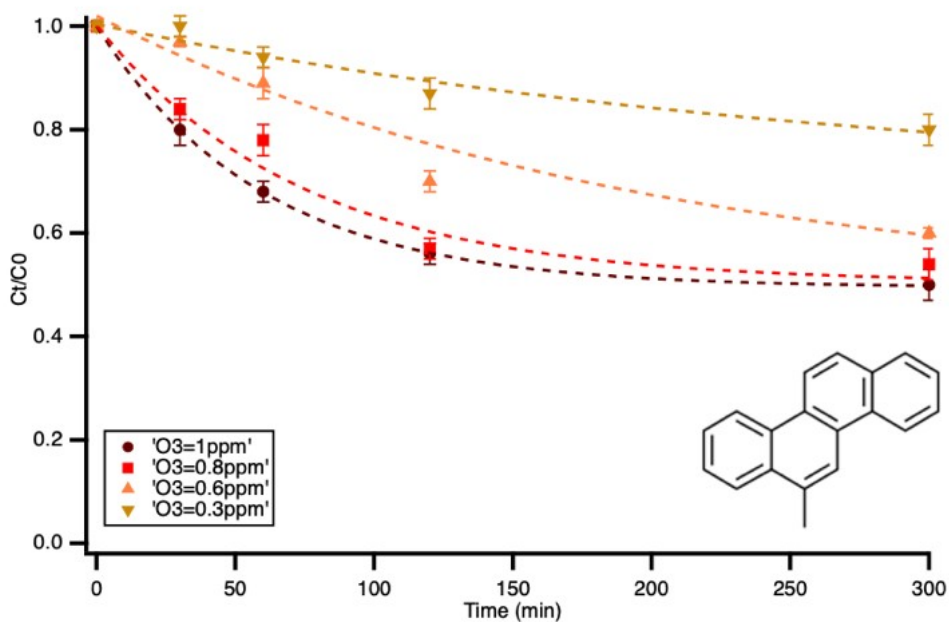
61 S2. Heterogeneous Oxidation Kinetics of 6-methylchrysene and 6-ethylchrysene

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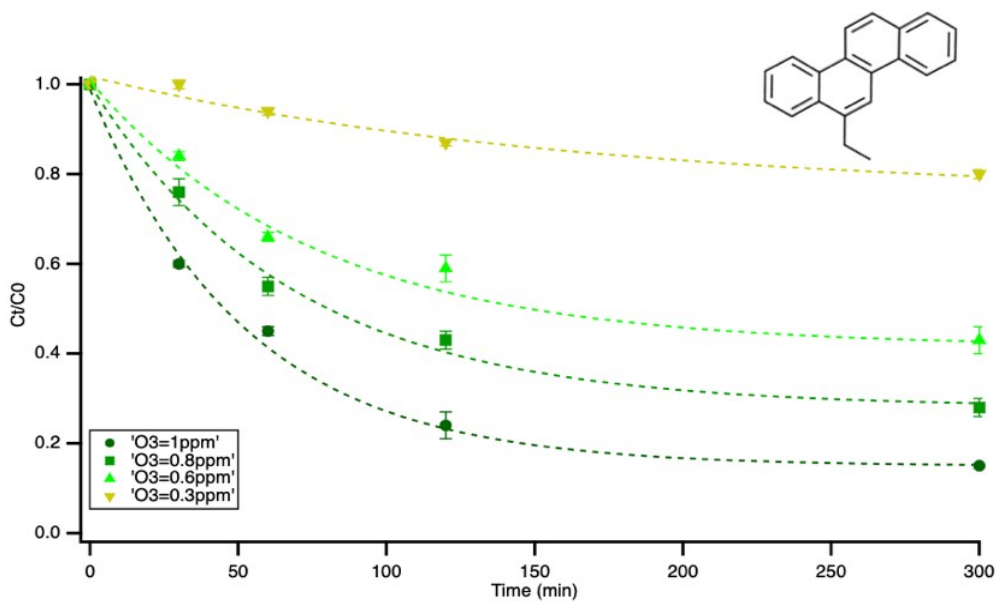
64 Figure S3 and S4 illustrates the decay of 6-methylchrysene and 6-ethylchrysene at varying ozone  
65 concentration with exposure time fitted with a first-order exponential fit. Unlike chrysene, the  
66 alkylated analogues do not show the oxidation delay at 30 mins.

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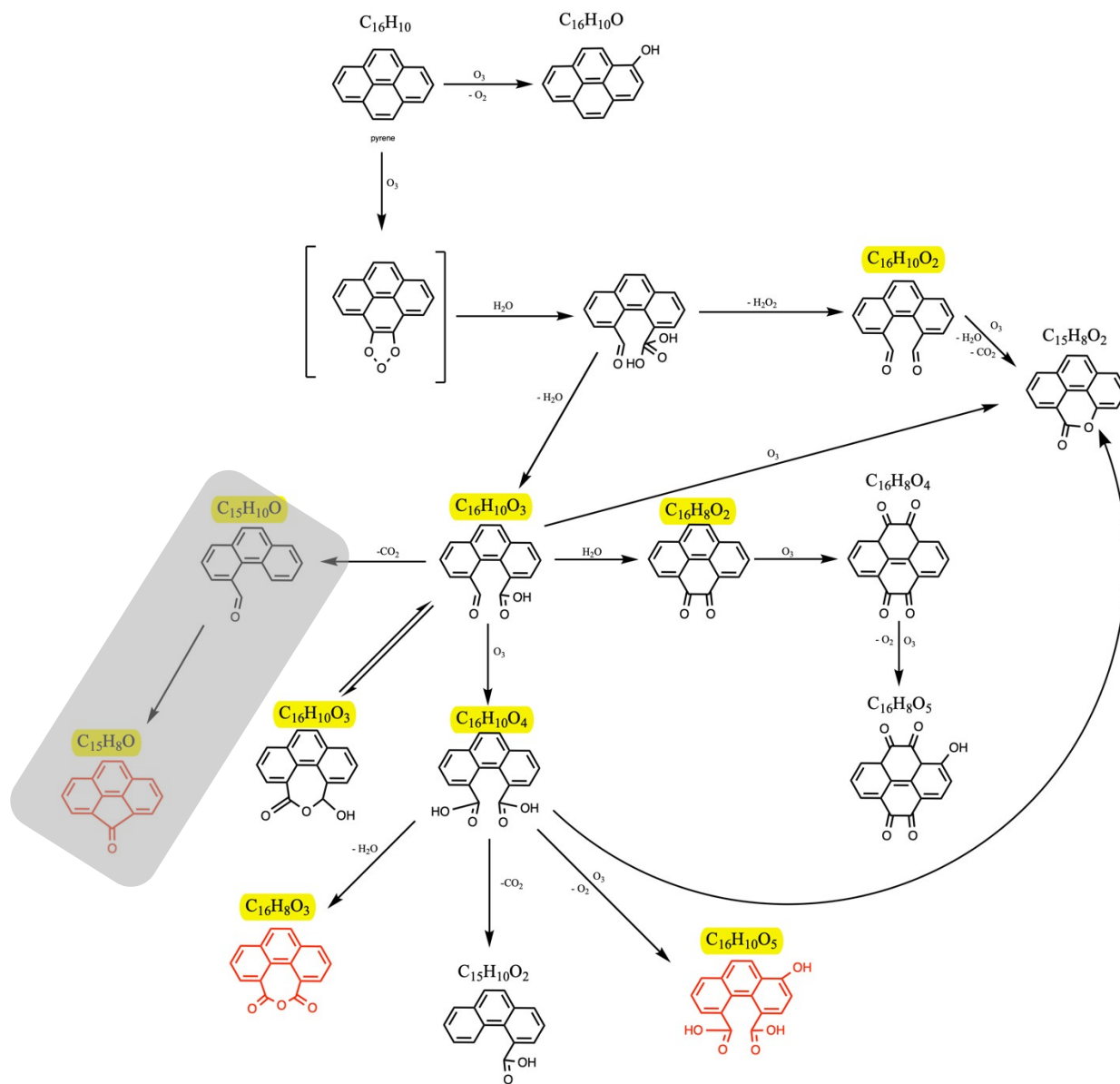
69 Figure S3. Evolution of 6-methylchrysene concentration with exposure time to 1,0.8,0.6 and  
70 0.3ppm of ozone with double exponential fit



71  
 72 *Figure S4. Evolution of 6-ethylchrysene concentration with exposure time to 1,0.8,0.6 and*  
 73 *0.3ppm of ozone with double exponential fit*  
 74

75 S3. Oxidation products

76  
 77 Figure S5 shows the mechanism for pyrene oxidation from the literature with minor changes to  
 78 include compounds detected in this study but not in the literature. The gray portion is likely a  
 79 result of fragmentation in the ESI source of the instrument, rather than during oxidation.  
 80



— Previous studies (Cochra et al., 2016; Miet et al, 2009; Qi et al, 2019)

— This study

**C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>** Detected in this study for pyrene

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82 *Figure S5. Proposed mechanism of pyrene oxidation adapted from studies by Cochran et al.*

83 *(2016), Miet et al. (2009) and Qi et al. (2019)*

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## 85 References

- 86 1. R. E. Cochran, H. Jeong, S. Fisseha Derseh, A. Gowan, J. Beránek, A. Kubátová, *Atmos.*  
87 *Environ.*, 2016, 128, 92-103. DOI: 10.1016/j.atmosenv.2015.12.036
- 88 2. K. Miet, K. Le Menach, P. Flaud, H. Budzinski, E. Villenave, *Atmos. Environ.*, 2009, 43  
89 (24), 3699-3707. DOI: 10.1016/j.atmosenv.2009.04.032
- 90 3. X. Qi, X. Pang, Y. Hong, Y. Wang, S. Lou, J. Feng, P. Cheng, Z. Zhou, *Chemosphere*,  
91 2019, 234, 608–617. DOI: 10.1016/j.chemosphere.2019.06.050

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