

## ***Interactive comment on “Organic peroxy radical chemistry in oxidation flow reactors and environmental chambers and their atmospheric relevance” by Zhe Peng et al.***

**Anonymous Referee #1**

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This paper follows a number of others reporting the characterisation and optimisation of operating conditions for oxidation flow reactors (OFRs) through both experimental and modeling studies. This work focuses on a model study of the fate of organic peroxy radicals within OFRs under different operating conditions and makes comparisons to the fates of such species in the atmosphere. While the rationale for such a study is sound, and the methods described are appropriate, the paper is quite long for the information it contains, and there are questions as to the wider interest and novelty of the work. It would help if the authors could state the main scientific outcomes and objectives of this work more clearly, and if some detail could be provided which outlines how assumptions regarding the fates of RO<sub>2</sub> species have potentially impacted the

C1

results of previous studies.

Specific comments are listed below.

Page 4, lines 117-122: Is production of RO<sub>2</sub> from ozonolysis reactions or reactions between O(1D) and VOCs considered for conditions when significant ozone/O(1D) are present? Although photolysis of organics is considered, is there any consideration of photolysis of oxygenated VOCs (formaldehyde or acetaldehyde for example) which may photolysis to generate RO<sub>2</sub> radicals?

Page 4, lines 133-134: The authors assume average ambient HO<sub>2</sub> concentrations of 1.5x10<sup>8</sup> molecules cm<sup>-3</sup> and k<sub>HO2+RO2</sub> of 1.5x10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The generic rate coefficient for HO<sub>2</sub> + RO<sub>2</sub> used seems high, for HO<sub>2</sub> + CH<sub>3</sub>O<sub>2</sub> the rate coefficient is 5.2x10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, while that for HO<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> is 6.9x10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. How do the assumptions regarding [HO<sub>2</sub>] and k<sub>HO2+RO2</sub> influence the results reported in this work? Similarly, how does the assumption regarding k<sub>RO2+NO</sub> influence the results?

Page 4, line 152 (and elsewhere): Please consider changing ‘RO<sub>2</sub>s’ to ‘RO<sub>2</sub> radicals’ or similar.

Page 5, line 175: Please quantify the statement ‘acylperoxy nitrates barely decompose’ with an example.

Page 6, line 205: What is the rationale for this production rate of OH? What is the VOC concentration used? (i.e. What is the pseudo-first-order rate coefficient?)

Page 6, line 220 and page 10, line 370: Are the results from these simulations reported anywhere? How is this estimate achieved?

Page 8, line 304: I’m not sure forested areas should be described as ‘low VOC’ given high biogenic emissions in such regions.

Page 9, line 307: Are the labels C1, C2 etc. shown in the Figures described anywhere?

C2

Page 12, line 421: Subscript in 'RO2'.

Page 13, line 490: Should this read ' Neither is the fast RO<sub>2</sub> + RO<sub>2</sub> ...'?

Page 16, line 585: Please provide a reference to the statement '... other major gas-phase radical reactions have weak or no temperature-dependence' or compare to a typical change in rate coefficient over a similar temperature range for RO<sub>2</sub> + NO, RO<sub>2</sub> + HO<sub>2</sub> and RO<sub>2</sub> + RO<sub>2</sub>.

Page 16, lines 599-611: The utility of the RO<sub>2</sub> fate estimator is unclear. What does it do above and beyond a simple yield/budget calculations requiring knowledge of [HO<sub>2</sub>], [RO<sub>2</sub>], [NO] and the corresponding rate coefficients? It would be surprising if groups performing OFR studies, or similar, weren't already able to do such calculations.

Figure 1: The labels C1, P1, U etc. are unclear and/or overlapping with other labels on the plots.

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C3