

Pereira et al. presented a chamber operated in continuous mode (CFR) with conceptually the same photochemistry initiating method as the “OFR185” operation mode of oxidation flow reactors (OFRs) (George et al., 2007; Kang et al., 2007; Lambe et al., 2011; Li et al., 2015). They used their CFR to produce very large amounts of SOA for a suite of offline physicochemical analyses, including some requiring high OA amounts. Although the inlet was well controlled and the offline analysis was comprehensive, the reactor and experiment design have a couple of fundamental problems. These are so major that it is unclear to me whether the paper should be published, unless the issues are described thoroughly and the paper used to describe an incremental design step that was not quite successful, which will be built upon to achieve a more atmospherically-relevant reactor in a future iteration.

(1) Although the volume being larger than OFRs is touted as an advantage of the CFR and part of its novelty, this apparent advantage is negated by the distribution of UV light and species of interest, which appears to be extremely heterogeneous. A pen-ray was used as the light source in the CFR. Although the authors did not specify the dimension of its lighted area in the paper, I searched for this information on the website of its manufacturer (<https://www.uvp.com/mercury>) and it would appear that it is very small (lighted length as small as <2 cm). Even if it is slightly larger than that, the pen-ray can be roughly regarded as a point light source given the large volume of the CFR. Then the photon flux scales inversely with the square of the distance to the light source. Let’s assume that a spherical UV source with a diameter of 5 cm (much larger surface area than a stick-like lamp with a lighted length of 5 cm). Then there is only 1% of the initial UV intensity (next to the lamp) only ~20 cm from the pen-ray surface under the assumption of no light absorption, and only 0.08% of the initial intensity near the corners of the reactor (assuming the UV light placed right in the middle of the reactor). The UV absorption at 185 nm by O₂ exacerbates this problem. O₂, with a cross section of ~10⁻²⁰ cm² at 185 nm, only needs a ~20 cm optical path to reach an optical depth of 1. This leads to an additional e-fold decay of the intensity every 20 cm, *in addition* to the intensity decay caused by the geometry. When applying this effect, the light remaining at 20 cm and the reactor corners is 0.6% and 0.0008% of the initial values, respectively. 99.5% (93%) of the reactor volume has light intensities smaller than those near the light by a factor of 10 (100).

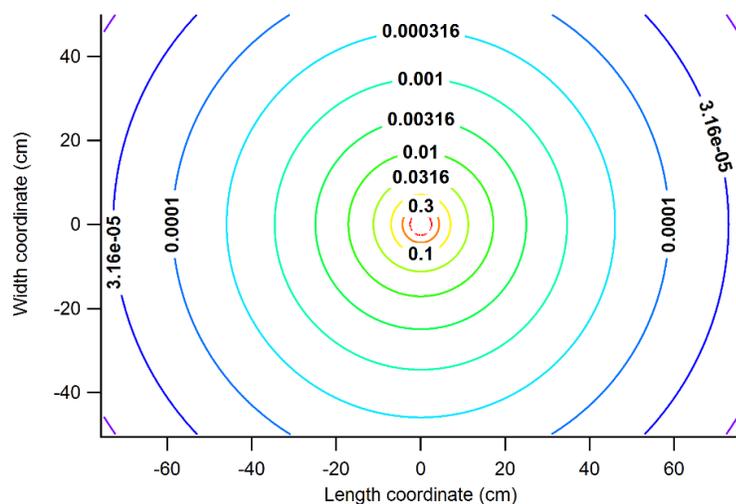


Figure: Contour plot of the estimated field of 185 nm UV intensity relative to that at the lamp surface in the horizontal section cutting the center of the lamp, under the assumptions of i) a spherical UV lamp with a diameter of 5 cm ii) placed in the center of the CFR, iii) O₂ cross section at 185 nm of 1x10⁻²⁰ cm² and 1 atm of air pressure, and iv) absorption of the 185 nm light by the reactor surfaces. The lamp center is set as (0, 0).

Therefore, despite its larger volume than most OFRs, most of the volume in the CFR seems to be photochemically “dark” and its photochemically useful volume is actually smaller than common OFRs, e.g., PAM and CPOT (in almost the whole internal space of PAM (volume: ~13 L) for all commonly used lamp placements, the relative 185 UV intensity to the lamp surface is >5% (Peng et al., 2018), while for the case discussed above, the volume with a relative 185 nm UV>5% is only ~3.5 L). Thus despite its large volume, this is a very small effective reactor.

Even within the photochemically active space, UV intensity still varies substantially, which makes it difficult to relate offline analysis results to a certain reaction condition. Then the results of the offline analysis are less informative.

I suggest that in the future the authors use multiple lights in a better layout to make the UV field as uniform as possible. This would lead to more uniform conditions and the production of more meaningful SOA material.

(2) The experiments were conducted using tens of ppm of VOC and several ppm of NO_x, corresponding to OH reactivities of thousands of s⁻¹ and more (ranging from ~3,000 s⁻¹ for Exps. 34 and 35 to ~300,000 s⁻¹ for Exps. 26-28). These extraordinarily high reactivities are certain to reduce OH concentration in the CFR by several orders of magnitude (Peng et al., 2015). But UV intensity at 185 and 254 nm is not reduced by the addition of the VOCs, and could play a major role in VOC loss compared to reactions with OH (Peng et al., 2016), especially for toluene, which strongly absorbs at 185 and 254 nm.

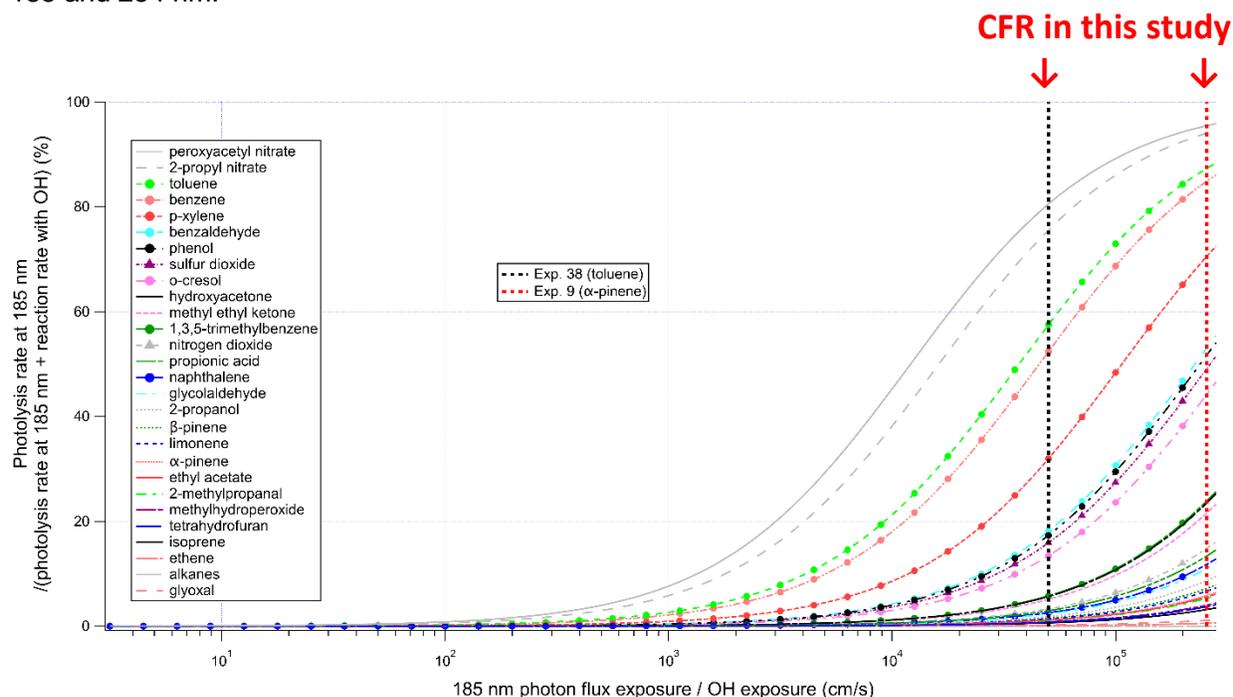


Figure: plot to quantify the relative importance of 185 nm VOC photolysis to their reactions with OH in same format as Fig. 1 of Peng et al. (2016). The x-axis positions of Exps. 9 and 38 are estimated using the OFR Exposure Estimator (<https://sites.google.com/site/pamwiki/hardware/estimation-equations>) under the assumption of a uniform 185 nm UV of 1×10^{13} ph cm⁻² s⁻¹ in the CFR. That of Exp. 28 has also been estimated. Its value is too large (~ 1×10^7 cm/s) to be shown in the plot, and would be

expected to be so large that many molecules would have their fate impacted or dominated by 185 nm photolysis.

Energetic 185 and 254 nm photons may result in a very different organic radical chemistry than in the atmosphere and typical chamber experiments. Although the authors claimed that their objective was not to perfectly mimic atmospheric conditions, clearly a key goal is to produce SOA that is atmospherically-relevant. For example, they repeatedly compared their offline analysis results to ambient measurement and chamber experiment results in the literature as validations of their experiments. If the CFR was only to produce SOA to test several offline analytical instruments with a complex mixture of oxidized species, the current CFR experimental design is purely a laboratory exercise and viable as such. If the authors assume that their CFR-produced SOA may serve as surrogate of ambient and/or typical chamber SOA to any extent (even though the experimental conditions do not replicate ambient conditions), the unrealistic photochemistry initiated by 185 and 254 nm UV should be avoided. In the experiments reported in this paper, OH was always substantially reduced by VOC and NO_x. Thus most of the SOA samples shown in Fig. 5 were only weakly oxidized. Toluene-derived SOA was an exception because strong photolysis at 185 and 254 nm may have produced more organic radicals (followed by O₂ addition etc., leading to higher O:C). Those photolysis products were likely to be smaller and more volatile, and have lower SOA yields. The peculiarity of toluene experiments suggests the importance of strong 185 and 254 nm VOC photolysis occurring.

If the authors intend to claim any relevance of CFR-produced SOA to ambient and/or typical chamber SOA, they have to limit the amount of VOC (and NO_x) injected to avoid the above problem. OH reactivity of tens of s⁻¹ has been recommended for similar reactors using the same OFR185 photochemistry, in order to maintain the chemistry in a tropospheric-relevant regime (Peng et al., 2016; Peng and Jimenez, 2017). **This is 100-10000 times lower than the reactivities used in this paper.** Assuming a VOC reacting with OH at 10⁻¹¹ cm³ molec⁻¹ s⁻¹, roughly 100 ppb of VOC can be injected into the reactor without entering conditions with significant 185 or 254 nm VOC (and product) photolysis. Then this is roughly the upper limit of OA that can be made in OFRs (including the CFR) using Hg lamps to generate OH. **This is about 100 times lower than the concentrations used in this paper.**

In this sense, if the authors do not employ multiple lights to largely make use of the volume of the CFR, its SOA production capacity is not superior to other OFRs (e.g., PAM). There have already been a number of papers where other OFRs were used to produce SOA that was deposited on substrates and collected on filters, for SFG and viscosity analysis, respectively (e.g., Shrestha et al., 2015; Song et al., 2016). Besides, PEAR, a large OFR, has been recently presented and appears to have a more appropriate design for the purpose of producing SOA in large quantities (Ihalainen et al., 2018). Thus I do not think that OFR (CFR) as a tool to produce larger concentrations of SOA (by collecting over a longer period of time) is really a novel concept.

Specific comments:

Page 3, Line 30: OFRs (e.g., Aerodyne PAM) also have good flow and precursor injection control.

Table 1: there was no really low-NO_x experiments among those with NO_x injected in Table 1. Even with a VOC:NO_x ratio of 13, NO_x was still injected in ppm. Compared to HO₂ (not VOC), NO_x should have always dominated RO₂ fate in the CFR experiments reported in this paper.

Section 2.3: although offline analysis methods are not the main focus of this paper, a brief description of potential artifacts in these offline analyses would still be helpful.

Technical corrections:

Figure 1: please change the bag volume from “3 m³” to “0.3 m³”.

Page 14, Line 5 and Page 19, Line 10: references Cao et al. and Shrivastava et al. are missing in the reference list.

Page 14, Line 7: please add “of” after “intensity”.

Page 19, Line 33: is “Although a faster evaporation rate...” a part of the preceding sentence?

Page 20, Line 10: the word “bin” is missing after “μg m⁻³”.

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