**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "A laboratory flow reactor with gas particle separation and on-line MS/MS for product identification in atmospherically important reactions" *by* J. F. Bennett et al.

Anonymous Referee #3

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This manuscript describes the development of a flow reactor to be interfaced with a mass spectrometer that facilitates separate analysis of aerosol trace gases and particles. Understanding gas-to-particle exchange in an aerosol parcel is critical and the utility of this reactor is evident, as shown in its application to product analysis of xylene oxidation. While the manuscript is written clearly, there are areas of interpretation that could be further developed and clarified in order to more fully understand the capabilities of the reactor. Additionally, it would be helpful to indicate limitations on its use. I recommend publication of the manuscript following revisions suggested below.

Specific Comments:

p1354 line 20. The ionization methods referred to tangentially should be defined explicitly (photoionization, electron impact ionization). Additionally, two-step laser desorption/ionization schemes exist that minimize fragmentation of organics (e.g. Woods et al. *Anal. Chem.* 73. 2317-2322)

p1357 line 5. 6ppm of NO is a very high NOx environment to be making kinetics measurements and examining ambient chemistry in. Even by eliminating photolytic formation of O3, I would think that this would influence the resulting chemistry. Is there any evidence in the spectra that these compounds are not changing the results? Since ambient O3 was present in the air used. what about HNO3 formation? Sulfate in particles? What effect does

p1360 line 6-9 The hypothetical loss rate of 0.12% s^{-1} over a residence time of 4.5 min * 60 sec/min = 270 sec seems to yield a larger loss than the reported 10%. Since particle size changes with SOA chemistry this instrument will effectively filter the population of aerosol that the MS samples. Comparison of PSD of xylene reaction products before and after denuder?

p1360 line 15-16 What is the APCI's limit-of-detection toward the target analyte xylene? Approximately (order of magnitude) how many aerosol particles get averaged into a typical mass spectrum?

p 1361 line 2-3. I have never encountered circumstances in which charge transfer resulted in the formation of a molecular ion. Is there a reference that could be cited to support this interpretation? Could secondary chemistry, or EI be contributing to the ion signal?

p1364 line 4-5. In the absence of seed aerosol, xylene oxidation results in the nucleation of particles in the sub-10nm range that can then grow and/or agglomerate over the 4.5min residence time in the reactor. Stripping of semi-volatiles from the con-

densed phase may also shift the measured size distribution of xylene-oxidation SOA. I think further support is necessary to argue that the 35nm Ammonium Sulfate particles are smaller than what is being formed in the reactor during xylene oxidation. Additionally, what is the mass balance of a test organic aerosol? It seems that the reactor influences the size, and based on what we know of SOA evolution this also influences the chemistry, of the aerosol particles introduced to the APCI.

p 1364 line 20-22. How is the resulting ion signal influenced by the heater temperature? Is there any difference in fragmentation, for example? And, why was 100C used and not 200C?

p 1365 line 8-9 A table of the primary peaks of the spectra, their fractional abundance, and presumed structures would be helpful. It is a little hard to tell the actual m/z of the peaks from the figure. Additionally, some explanation of the resulting mass spectrum from the unreacted xylene would be useful. Section 2.1.4 mentions that the primary ions produced with H_3O^+ CI are $(M+H)^+$ and clusters with water. However, in Fig 6c $(M+H)^+$ and $(M+H_2O+H)^+$ appear to be minor peaks. Was this spectrum sensitive to parameters like vapor pressure of H_2O used, etc.? Explanation of this spectrum would also help support product peak assignments.

p1365 line 26-28. As noted above, can you be sure that m/z 122 is really M^+? Given how much of the ion signal for xylene was above m/z = 107, couldn't this be a fragment of a larger species? Figures 7-9 show only MS/MS spectra so it isn't clear whether m/z = 122 is the predominant peak in the MS spectrum.

p1366 line19-21. Would changing the flow rate through the cell allow you to determine the origin of the signal? Additionally, would this allow you to estimate gas-particle partitioning of semi-volatile species more quantitiatively?

p1368 line 15. The conclusions could be developed more. What sort of conditions would this reactor work well for (i.e. better for investigating more aged aerosols since nucleated particles at early reaction times are likely to be completely stripped by the

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reactor)? Reaction conditions involve high levels of NOx, how does this influence the results? In what further ways could the instrument be used to investigate key physical parameters of an aerosol like volatility, etc.?