

***Interactive comment on* “Temperature effect on physical and chemical properties of secondary organic aerosol from *m*-xylene photooxidation” by L. Qi et al.**

Anonymous Referee #1

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The authors investigate temperature effects on the composition and overall secondary aerosol mass yield from *m*-xylene photooxidation. This is a very interesting paper reflecting careful and comprehensive experimental work. The central argument of the paper is that gas-particle partitioning theory alone is not sufficient to explain observed differences in the SOA, and while the data are very intriguing it is not obvious to me that this conclusion is supported by the data.

My summary of the findings is as follows: when SOA in the very large UCR chamber is heated up after being formed under cool conditions, a fraction of the SOA evaporates and a number of observables reflect that evaporation, all consistently. When instead

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SOA is formed under warm conditions and the chamber is later cooled, there is relatively little change in the SOA, though themodenuder data do suggest a slight addition of relatively volatile material from the gas phase. The suite of observations include SOA volume (which drops upon warming but does not rise much after cooling), density (ditto) hygroscopicity (ditto but it increases upon warming), thermal volatility (thermodenuder volume fraction remaining), which shows a sharp rise in VFR after heating but a more modest decline after cooling, and AMS spectra, which change significantly after heating but are essentially unchanged after cooling.

From these observations the authors conclude that the SOA formed at lower and higher temperature is fundamentally different – i.e. that either the gas-phase or secondary condensed phase chemical mechanism is strongly temperature dependent. This could well be true; what we do know about aromatic mechanisms certainly supports extensive and complex multi-generational chemistry. They also argue that gas-particle partitioning theory can not explain their data. I don't agree.

My issue here is that I believe that an equally plausible argument can be made that the chemistry under the two sets of conditions is fundamentally similar, and that rapid gas-phase reactions effectively sweep out the semi-volatile vapors but leave behind relatively volatile condensed-phase constituents. The resulting particle-vapor suspension would have relatively little material with volatilities resulting in highish vapor fractions ($K_o M_o \geq .1$, say) but plenty with only modestly lower volatility. Warming by 35K would cause this material to evaporate, driving the observed changes (and indeed, when the SOA is warmed all of the observables move toward the values they have when formed at lower T). There is nothing about gas-particle partitioning theory that says that the gases have to be there in substantial quantities – the theory only requires that if they are there the partitioning will follow equations 1 and 2.

It would be very interesting to know what happens when SOA is formed at 278 K, the lights are turned off, and the chamber is then sent through a cycle of warming to 313K and then cooling back to 278K. THAT would at first blush appear to put partitioning

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theory to the test.

The authors should discuss their argument in the context of what we do know (and do not know) about the xylene mechanism.

The thermal behavior of aromatic SOA (44 increasing after heating) has also been reported by Hildebrandt et al for toluene SOA.

The fig 5 y axis should be rescaled. The AMS community has adopted a standard practice of normalizing to the total mass signal, not the highest peak (in other words, the 43 and 44 signals would indicate the percentage of the total organic signal at those masses. This is a more informative axis and a lot of researchers have developed an intuition around it – there is no reason not to use it. Likewise, a discussion of the fragmentation table values used to obtain these unit mass resolution spectra should be included.

There is no discussion here of the aerosol mass yields. While that is not the principal focus, it is none-the-less the single property of most interest to the air-quality modeling community and it should be addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 863, 2010.

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