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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Inferring ozone production in an urban atmosphere using measurements of peroxynitric acid" *by* K. M. Spencer et al.

Anonymous Referee #2

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This paper uses mass spectrometric measurements of peroxynitric acid HO2NO2 taken aboard the C-130 aircraft during the MILAGRO campaign to make inferences about the local rate of ozone production. Specifically, it is shown that HO2NO2 can be used as a surrogate for HO2, since the two species are in a rapid equilibrium. The inferred values of HO2 are then used to estimate the instantaneous ozone production rate, since this quantity is related to the amount of NO2 produced from RO2/HO2 + NO.

The paper falls in the territory between a brief letter and a detailed full paper. Details on such vital information as the temperature and water vapor are missing, as

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are specifics about NO, OVOC, OH, etc, which would make it easier to interpret the paper. I would recommend eventual publication of the paper after addressing some issues about its organization and content. The actual measurements of HO2NO2 are novel and valuable, and should be the major focus of the paper. The measurements of ozone production rate are more uncertain, though, and I suspect they may be a little overinterpreted.

The major premise of the paper is that HO2NO2 is linearly related to the HO2 concentration. However, the temperature is not given for the measurements (only a 50-degree range). I was able to figure out from other papers that the 3/29/06 flight, which is highlighted, was mostly at low altitude, and hence warmer temperature; but it would be nice to know this to be able to calculate the rate of cycling between HO2NO2 and HO2.

Specific comments

Page 2798 and Figure 2. It looks to me like the slope of the fit line is around 0.75 (380/500), not 0.90 as stated. This means that transitioning from wet air to dry air could introduce an uncertainty of 25% into the measurements. This could play a role in the low altitude flights mentioned above. Interestingly, the data on March 29th (red dots) all lie closer to the 1:1 line than to the robust fit line.

A brief look at the Shon et al. paper in the same Special Issue of ACPD suggests that he March 29th data had anomalously high photostationary states compared to other Boundary Layer runs. Does that impact the ozone production rates here at all?

Box model. How was acetaldehyde treated in the model? It is thought to be one of the major contributors to OH reactivity, and probably also to HOx production. Was the concentration allowed to be governed by the chemistry of larger alkanes, or was it constrained by in-flight measurements? This could affect the modeled concentration of HO2 dramatically. How is propene treated? It is not mentioned explicitly in the list on page 2800, but is a major precursor of acetaldehyde, and a contributor to OH reactivity.

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Page 2802 and Figure 5. To play Devils Advocate, the observed HO2NO2 at high NOx lies very close to the 1:1 line, while the majority of measurements lie closer to the 0.8:1 line. So, it is hard to justify the statement that the model underpredicts HO2NO2 concentrations at high NOx, when these measurements are in fact closer to the model than the majority. As I commented earlier, there is a possible 25% discrepancy between measurements obtained at low and high H2O, and these discrepancies clearly fall into that range.

Page 2802, lines 14-17. It should be clarified for the general reader that this refers to the instantaneous rate of photochemical ozone production, not the net rate.

Page 2803, lines 14-23 (first paragraph of Discussion). This paragraph is not particularly relevant (or correct). It seems to imply that HO2 cycling mostly occurs through alkanes, where there is an alpha-hydrogen attached to the carbon bearing the alkoxy radical. As was shown in the TEXAQS campaigns, the most potent sources of ozone are typically alkenes. Here the OH adds to the hydrocarbon, leading to alkoxy radicals of the form HOCH2CH2O, which decompose to form CH2OH, and then give HO2. Conversely, for many alkanes, despite the presence of an alpha hydrogen atom, the alkoxy radical decomposes. This process tends to lead to 3 (NO to NO2) conversions. So, I am not sure where that paragraph is leading. If all the RO2 are being accounted for explicitly, it does not matter whether they have alpha-hydrogen atoms or not. However, if you are trying to predict the number of NO2 formed per OH produced, then the number of conversions matters, for the above reasons. Also, I am not sure what tertiary aldehydes are, or how that fits in.

Figure 8. There does seem to be a slight tendency for the P(O3) values to fall off in the model, but I am not convinced that it is that much different from the observations, or that you can be sure that the production rate of HOx is constant in reality, since the relative amounts of secondary carbonyls can change. Looking at Figure 7, it seems like the largest discrepancies actually occur at low NO, where the measured values of P(O3) span 2 orders of magnitude. Again, on line 16 of page 2804 it is stated that

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observed HO2NO2 levels are greater than the model at high NOx, whereas in fact they lie close to the 1:1 line in Figure 5.

Page 2806, discussion of sources and sinks. These are good tests as to the sensitivity of the ratios to different kinetic parameters. It is not clear how HOONO was treated, since the 2006 JPL evaluation treats this as an explicit channel. Depending if HOONO regenerates HOx or serves as a sink, it can affect the overall HOx loss rate. Please give more explicit details about this.

The caption to Figure 9 could be more complete. It needs to say what is plotted on the y-axis i.e., ratio of calculated values of HO2NO2 using different values of the following parameters.

Typos: Page 2805, line 8. where should be were. Page 2810: Lurmann et al. reference, page numbers should be 10905-10936.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 2791, 2009.