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Comment

Interactive comment on “Intercomparison of peroxy radical measurements obtained at atmospheric conditions by laser-induced fluorescence and electron spin resonance spectroscopy” by H. Fuchs et al.

H. Fuchs et al.

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We thank the referee for his/her review and useful comments. Listed below are our responses to the comments and changes made to the revised manuscript.

Comment The ROxLIF sampling inlet was approximately 87 cm above the floor of the chamber, while the MIESR inlet was approximately 2 cm above the floor of the chamber. Since the methane photooxidation experiment involved radical production through the photolysis of HONO and HCHO produced at the surface of the reactor, could there be a radical gradient from this process leading to higher peroxy radical concentrations near the walls of the reactor? Similarly for the ozonolysis experiments,

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could heterogeneous effects affect peroxy radical levels near the walls of the chamber? Providing additional evidence that the radical levels measured in the chamber are consistent with expected values based on the source strengths of the radical precursors, perhaps through a modeling effort, would improve confidence in the measurements.

Response To our knowledge, the mixing within the chamber is sufficiently fast that there are no gradients of radical concentrations. Operation of a fan ensures turbulent mixing within 1 minute. The photolytic lifetime of species producing radicals in the methane oxidation experiment was much longer (20–40 minutes for HONO and 5–7 hours for HCHO) so that no concentration gradients were expected. During the ozonolysis experiment the lifetime of radicals is again larger than the mixing time (in the order of 5 minutes). The sufficient mixing is also supported by a previous intercomparison experiment of two OH instruments in the chamber. In this experiment OH was measured by the LIF instrument, which sampled 2 cm above the floor in the configuration used for OH measurements, and by the DOAS instrument, which measured the averaged OH concentration along the long symmetry axis (center line) of the cylindrical shaped chamber (Schlosser et al., *J. Atmos. Chem.*, 56, 187–205, 2007). No systematic difference due to concentration gradients was observed. We added to clarify this point on p. 384: "Turbulent mixing of the chamber air ensures that the relatively short distance between sampling point and chamber surface does not lead to gradients in the radical concentrations, which would affect the intercomparison (Schlosser et al., 2007)". The focus of this paper is the comparison of measured radical concentration and we decided not to include model calculations. Comparison of measured and modeled concentrations would be rather useful to test the model than to support these measurements. This would be published elsewhere.

Comment Decomposition of Criegee intermediates inside the low pressure FAGE cell could lead to the production of OH radicals, resulting in an interference in the LIF measurements. Did the authors observe such an interference in their experiment, perhaps providing an upper limit to this potential interference for OH field measurements using

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the LIF-FAGE technique?

Response The lifetime of excited Criegee intermediates produced in the ozonolysis reaction is not exactly known, but most likely very short. For example, the Master Chemical Mechanism (MCM, University of Leeds) assumes an instantaneous decomposition of excited Criegee intermediates once they are produced. Thus the steady state concentration of these intermediates is expected to be much smaller than that of the resulting peroxy radicals. A contribution to the ROxLIF signal is therefore not expected. Stabilized Criegee intermediates may live longer. Their yield in the ozonolysis of 1-butene is likely approximately 20 % (Jenkin et al, Atmos. Chem. Phys., 3, 181-193, 1997). The stabilized Criegee radicals will be scavenged and converted to non-radical products (aldehydes, CO₂) by the large amounts of CO in the SAPHIR chamber and in the ROxLIF reactor (S. Hatakeyama et al., Res. Chem. Intermed., 20, 503-524, 1994). Thus, it is justified to assume that neither excited Criegee nor stabilized Criegee intermediates would be detected by ROxLIF during this experiment. Unfortunately we cannot specify the potential interference in the OH measurement during this experiment. We edited the text on p. 388: "The stabilized Criegee intermediates react with the large excess of CO initially injected into the chamber to corresponding aldehydes and CO₂ (Atkinson, 1997, Hatakeyama et al., 1994). The large amount of CO also converts OH completely to HO₂ and prevents possible reactions of OH with 1-butene and its ozonolysis products. Thus, the chemical system is expected to produce C₂H₅O₂ and HO₂ as the only peroxy radicals in the chamber. Interferences of the ROxLIF measurement from Criegee intermediates are not expected in these experiments. The excited Criegee radicals from the ozonolysis reactions are short-lived intermediates in the formation process of the peroxy radicals, and as their chemical lifetime is very much shorter, their concentrations are negligible compared to those of the peroxy radicals (Jenkin et al, 1997). Stabilized Criegee radicals also do not play a role, because they are efficiently scavenged and converted to non-radical products by the high concentration of CO in the SAPHIR chamber and in the ROxLIF converter (Atkinson, 1997, Hatakeyama et al., 1994)."

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Comment What factors contribute to the variation in the precision of the ROxLIF instrument during these experiments (Figures 1 and 2). Why was the precision of the MIESR measurements better during the ozonolysis experiments?

Response Figures 1 and 2 show 5 min average values of the ROxLIF instrument as mentioned in the captions and error bars are 1σ standard deviations. This error reflects the precision of the measurement and the variability of short-living radicals within the integration time. However, the variability of radical concentrations was small for most of the time. This holds especially for the ozonolysis experiment except for transitions from one to the next concentration level. Error bars of some data points in the methane oxidation experiment are obviously influenced by the variability of the radical concentrations within the 5 min interval, as can be seen from the variability of the HONO photolysis frequency (also shown in Figure 1). Since RO₂ radical concentrations are calculated from subtraction of two measurements, RO_x and HO_x, the precision of these values is reduced compared to HO₂. The precision of the MIESR measurement is determined by the noise of the measured ESR spectrum. The difference in the precision of MIESR measurements between both experiments reflects the day to day variability of the spectrometer's performance and is within the expected range.

Comment Page 377: In addition to hydrogen abstraction, OH and NO₃ can also add to the double bond of alkenes, leading to hydroxyalkyl peroxy radicals and other more complex peroxy radicals.

Response We are aware of these mechanisms, but do not want to expand the description of well-known atmospheric chemistry. Therefore, we canceled the line "which abstract H-atoms from hydrocarbon molecules, analogue to OH reactions," (page 377).

Comment Page 378, line 6 should read "...on the order of 10 pptv..."
line 12 should read something like "...in specially designed 64258;ow reactors for calibration."

line 20 should read "...the MIESR sampler was no longer available..."

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line 20-21 should read "...will be no longer be available..."

Response We thank the author for finding these errors and corrected them in the text.

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