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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.

Anonymous Referee #1

Received and published: 9 January 2009

This paper presents an intercomparison of peroxy radical measurement techniques under controlled chamber conditions using both Matrix Isolation Electron Spin Resonance (MIESR) and a new technique involving chemical conversion of RO_2 and HO_2 radicals to OH and subsequent detection of OH by laser-induced fluorescence (ROX-LIF). The latter technique has been extensively calibrated and characterized in a previous publication, but the agreement between the two fundamentally different techniques described in this paper provide additional confidence in this new technique. The authors conducted three different experiments - one using the photolysis of HONO as the

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radical source with both instruments operating at the same time, and two experiments using the ozonolysis of 1-butene as the radical source, with the MIESR instrument measuring during the first ozonolysis experiment and the ROxLIF instrument measuring during the second. Although the two instruments were not operating simultaneously during the latter experiments, the authors have shown that the conditions in the chamber were similar, justifying the comparison.

The paper is well written and appropriate for publication in AMT after the authors have addressed the following comments:

1) 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, 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.

2) Decomposition of Creigee 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 the LIF-FAGE technique?

3) 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?

Minor comments:

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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.

Page 378, line 6 should read "...on the order of 10 pptv..."

Page 378, line 12 should read something like "...in specially designed flow reactors for calibration."

Page 386, line 20 should read "...the MIESR sampler was no longer available..."

Page 391, line 20-21 should read "...will be no longer be available..."

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 375, 2008.

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