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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxy radical observations over West Africa during the AMMA 2006 campaign: Photochemical activity in episodes of formation of convective systems on the basis of radical measurements" *by* M. D. Andrés-Hernández et al.

Anonymous Referee #2

Received and published: 2 March 2009

Reviewers Comments

This paper describes peroxy radical concentration data obtained using an airborne Peroxy Radical Chemical Amplifier instrument during its recent deployment as part of a large scale aircraft campaign over the African continent. During the campaign, the aircraft platform encountered several large convective systems that transported peroxy radical sources and sinks from the boundary layer to the free troposphere in

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addition to plumes associated with biomass burning. The data obtained in situ were compared to modelled concentration based on known radical chemistries and showed good agreement when taking the quoted error of the measurements into account. The data presented are interesting and show clear evidence for unexpected radical chemistry suggesting the existent of unknown radical precursors being uplifted to sampling altitudes in conjunction with NO resulting in photochemical ozone production in some cases, but not others.

The paper is generally well written and organized. The figures are clear and the number of figures is adequate. The development of new aircraft based instrumentation always contributes to advances in atmospheric science and therefore I think this paper contains enough important information and novel content to warrant publication. My main concerns with the paper are the authors often do not fully address the potential questions of a more casual reader or a reader who is familiar with atmospheric radical chemistry but not the operation of the PERCA instrument specifically. In addition, often the authors data shows interesting details about the photochemistry of this region but they fail offer even speculation as to the exact nature of the chemical players in this unique photochemical environment. Most of my specific comments address these three issues.

I therefore would recommend the publication of this paper in ACP after some corrections.

Specific comments

Abstract, Line 10. The phrase atmospheric layers should be changed to altitudes

Introduction, Line 1 The first sentence in the text refers to organylperoxy radical. The correct term is alkyl peroxy radical.

Introduction, Line 8. The phrase 30 degrees northern latitude should be changed to 30 degrees North to maintain consistency with the earlier part of the sentence.

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Experimental: Line 1-16 The authors describe the operation of the PERCA instrument used to make the measurements of HO2 + RO2 described in the paper, including operation of the instrument and uses terms and descriptions such as chain length, and amplification verses background modes. The reader is referred to another paper with respect to the instrument used in this study, but it would assist the casual reader of this paper to describe in more detail the operation of the PERCA instrument in order to understand the experimental terms used in this section. The design, operation and function of the PERCA instrument is well documented in the literature and a more detailed list of references to this fact should also be included (e.g. Cantrell and Steadman 1982, Cantrell et al. 1996, Clemitshaw et al. 1997). Of particular importance is reference to the recent deployment of these instruments on aircraft (e.g. Green et al. 2003 , 2006) as this is quite a new development in the measurement of radicals using the PERCA technique.

Experimental Section 2.1, Line 18. The authors claim that the NO2 standard used to calibrate the PERCA instrument was not stable due to high temperatures and humidity causing wall losses. Did the authors prove in lab based experiments that such temperature and humidity changes cause the fluctuations as they saw during the aircraft campaign? Also, what are the drawbacks and likely propagation of errors in using the mathematical method based approach they describe? This section need to be explained in considerably more detail.

Experimental Section 2.1, Line 19. The phrase possibly caused that does not make sense and should be reworded.

Experimental Section 2.3, Line 10 The authors describe that the trajectory densities were normalized to 1. I do not understand why this was necessary. This section should be clarified.

Results, Line 2. The text refers to the uncertainty in the HO2+ RO2 measurement. I could find no overall assessment of errors in the data presented here, only later on line

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77 of the results section. Presumable the associated error mentioned on line 77 was the same as that described here and was determined and described in a secondary paper. The percentage error of 45% should be quoted with references to direct the reader to how this error was determined.

Results, Line 12. The authors used the data from CO, HCHO and CO2 to determine the likely VOC concentration in the airmasses sampled. Although this procedure is fairly standard in the community, the casual reader would benefit from a more detailed description of why this is possible with suitable references.

Results, Line 23. The text describes peroxy radical reactions. These should be explained clearly with the use of equations, or reference to relevant reactions included in Appendix A.

Results, Line 28. The phrase in the presence of radicals is obsolete.

Results, Line 30 Data suggest an ozone production of 1.7 ppb per hour. This number should be put in context with literature data for similar studies.

Results, Section 3.1. As stated previously, equations showing or referencing the radical chemistry would benefit the casual reader.

Results, Section 3.1. Line 11-16 The data presented here are most interesting. The authors speculate on the existence of an unknown radical precursor, simultaneously emitted with NO. Clearly this is the only conclusion based on the data, yet the authors make no attempt to suggest a possible identity of this precursor. Did the authors attempt any scenario modelling i.e. suggest a possible identity for this radical precursor, and the concentrations necessary to cause the observed concentrations of RO2? Also, since the concentration of ozone is constant at the time where the concentration of RO2 and NO both increase, presumably the rate of production of RO2 must be larger its rate of loss through its reaction with NO, and subsequent photolysis of the resultant NO2 into ozone. This fast photochemistry should be discussed in more detail.

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Conclusions Line 14. The authors speculate that thunderstorms could produce HOx or radical precursors from VOC decomposition. How would this be possible? Once again, equations and or reference would help clarify the statement.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1585, 2009.

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