

Review of "An intercomparison of CH₃O₂ measurements by Fluorescence Assay by Gas Expansion and Cavity Ring-Down Spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) by Onel et al.

This paper reports on laboratory measurements of methylperoxy radicals (CH₃O₂) using two different instruments (FAGE and CRDS) and with the radicals generated by two different sources. Instruments were calibrated primarily by the observations of the second order decay of CH₃O₂, so this procedure is discussed in depth. The paper is well organized and reports the important features of the instruments, the experimental setup and the comparison of the measurements.

While the development of techniques for measurement of methylperoxy radicals is important, as is comparison of the different methods. It is unfortunate that the detection limits for the CRDS method are so large, and obviously, it will not be possible to apply this method to atmospheric measurements. Still laboratory studies of radical kinetics and mechanisms is possible. Also, other cavity approaches may improve the performance of this approach (CAPS, IBBEAS).

This paper is suitable for publication, but this reviewer would like the authors to consider some general and specific comments in the preparation of their final manuscript.

General comments.

Regarding the calibration of the FAGE, it was surprising that the water vapour photolysis method was not used at all conditions studied. This instrument has been deployed on aircraft, so sensitivities for OH and HO₂ were surely determined as a function of sample pressure. It is straightforward to make use of this calibration procedure at reduced pressures for methylperoxy radicals. The paper would be greatly improved by performing such calibrations for the two other chamber conditions. On the other hand, since there is a systematic difference between the two methods of calibrations at 1000 torr, and that the authors favor the water vapour photolysis method (indicating that perhaps the rate coefficient for methylperoxy radical decay, k_{obs} , should be reduced by 25-30%), it appears to this reviewer that perhaps the FAGE calibration factors for the 80 mbar and 100 mbar should be scaled by the ratio of the calibration factors for the two methods performed at 1000 mbar. If the rate coefficient is indeed in error, the CRDS calibrations should also be adjusted by the same factor. As stated in the paper, though, if both instruments rely on methylperoxy radical decay for their calibration, then the accuracy of the value for k_{obs} does not matter, if the same value is used for both. Perhaps some more discussion of this in the introduction of the decay method should be included in the paper. It was also not obvious from the paper what k_{obs} referred to, so suggest adding some text to indicate that it refers to the effective rate coefficient for second order methylperoxy radical decay that includes contributions from methylperoxy radicals reacting with HO₂, which is produced from R5b followed by the rapid reaction of methoxy radicals with oxygen. It is possible that this is what lines 31-34 on page 6 were trying to say, but it was not clear to this reviewer. Suggest rewriting this text and/or adding more information. Note that without radical wall loss, $k_{obs} = k_{5a} + 2k_{5b}$. It would be useful to add discussion on the impact of HO₂ wall loss on k_{obs} both in the present experiments, and in those used by IUPAC to arrive at their kinetic recommendations.

Regarding the three conditions for the intercomparison: why were these selected? Would it have made sense to perform experiments in air at a variety of pressures (say five) between 100 and 1000 mbar? It is not apparent why helium/oxygen mixtures were used. Suggest adding some more discussion of the reasoning for the selection of chamber conditions for the intercomparisons.

Clearly, analytical techniques for methylperoxy radicals are going to be useful in application to reactions of these radicals, such as R5 and R12. This paper states that studies of R5 kinetics will be

reported in another paper. The authors may wish to consider publishing the other paper first, since such results could have direct bearing on the results of this paper.

Specific comments.

Page 4, line 24, 31-33. Very high concentrations of chlorine, methane and acetone were used in these experiments. Have you verified that these high amounts do not affect the performance of the instruments through interferences or artifacts? If so, suggest adding a discussion of the tests that were performed.

Page 4, line 38 to page 5, line 5. Suggest giving the transit times in addition to the distances in describing the sample moving through the FAGE.

Page 4, line 11-12. Suggest giving units for $C_{\text{CH}_3\text{O}_2}$ and $S_{\text{CH}_3\text{O}_2}$ factors.

Page 6, equations 3, 4, and 5. Suggest using Δt instead of t in these equations.

Page 6, line 26. Suggest rewording "...does not stop the decay analysis...".

Page 6, lines 30-34. Suggest rewording (mentioned earlier) this discussion.

Page 7, lines 1 and 3. Suggest adding discussion of the fitting procedure used in this paper, both for the radical signal decays and the instrument comparisons.

Page 7, line 12. It is stated that "...wall losses are very small and can be neglected." Suggest adding an upper limit for the wall loss of CH_3O_2 and for HO_2 (since this bears on the decay of CH_3O_2).

Page 7, line 21-22. It appears that the exponent for the sensitivity should be "-9" rather than "-10" as shown.

Page 8, line 9. Suggest "...S2 and S3, respectively."

Page 8, line 30. Does the large amount of ozone affect the instrument performance?

Page 10, line 14. Is it not possible to keep the radical concentration stable for more than 5 minutes? Perhaps this sentence needs rewording.

Page 10, line 35. Suggest rewording "...potential small difference in wavelength compared to λ in the spectrum...". The meaning is not clear as written.

Page 12, line 28. It is not clear where the term "Allan-Werle deviation plots" originated. As this reviewer understands it, the original term was Allan variance, which was extended to include Peter Werle's name after his contribution of suggesting its use in analysis of tunable diode laser spectroscopy performance. After his death, it was suggested that the term be changed to Allan-Werle variance. Suggest this term be used here.

Page 13, line 7. Suggest adding some explanation why the acquisition rate was only 6.5 Hz. Is it not possible to have 1000 or more ring-down events per second? Perhaps give typical ring-down times. This is mentioned on page 14, line 20. Perhaps indicate how much the frequency could be increased.

Page 13, line 15. Could additional optical filters be added to minimize the impact of the 254 nm photolysis radiation?

Page 15, lines 9 and 11. While "gradient" to describe the slope of a linear fit is technically correct, usually the term "slope" is used.

Page 15, line 25. Suggest "...and hence calibration of the CRDS...".

Page 15, line 26. Suggest "...and the intercomparison is not affected by error in the rate coefficient...".

Page 16, Figure 6(a). The decay of the CRDS and FAGE signals do not show the same temporal behavior. It appears there is a low pass filtering of the CRDS signals. Suggest discussing this. "Linear fit" and "orthogonal distance algorithm" are mentioned in the caption. This should be discussed in the text, with appropriate references. Also include information how the fit errors were determined. In the caption suggest "Each point is a value averaged over 3 seconds." Same suggestion for captions of Figure 7 and 8.

Page 16-17, Figures 6, 7, and 8. The 80 mbar data are averaged for 3 seconds, while the 100 mbar and 1000 mbar data are averaged for 5 seconds. Suggest discussing the logic for selecting various averaging times in the text. For the intercomparison, would it not be better to average for 1 minute or more, and generate different radical concentrations by adjusting the concentrations of precursors and/or the lamp intensity, rather than use the decays to achieve different concentrations? Suggest discussing the logic of the experimental design in the body of the document.

Page 17, Figure 8 caption. Suggest "The measurements by FAGE are shown in red and the measurements by CRDS are plotted in black."

Page 17, line 33. Suggest "...FAGE detection cell (from 3.3 to 0.9 mbar when sampling from a pressure of 1000 mbar." It is not clear why three pressures are listed, or what the "respectively" refers back to. Suggest reworking this last sentence.

Page 18-19. For future reference, it is much easier for readers if the references are formatted as "hanging" paragraphs.