

***Interactive comment on* “Direct detection of OH formation in the reactions of HO<sub>2</sub> with CH<sub>3</sub> C(O)O<sub>2</sub> and othersubstituted peroxy radicals” by T. J. Dillon and J. N. Crowley**

**Anonymous Referee #2**

Received and published: 2 May 2008

This excellent paper reports direct measurements of the OH radical yields from the reaction between HO<sub>2</sub> and acetylperoxyl radical. That OH radical is produced in this reaction was reported in 2004 by Hasson et al. on the basis of end product analysis. Subsequent experiments by Jenkin et al. (2007) supported their interpretation, although LeCrane et al. (2006) disagreed. The present work reports direct laser induced fluorescence (LIF) measurements of OH radical under conditions that minimize the influence of secondary reactions, confirming the production of OH and reporting quantitative branching ratios. The present work also shows that OH is produced in reactions of HO<sub>2</sub> with two additional carbonyl-containing RO<sub>2</sub> radicals, but not in reactions with some others that do not contain carbonyl groups. The results presented

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



here are important because they show that RO<sub>2</sub> + HO<sub>2</sub> reactions are not always terminating, as had been thought previously.

The experiments were carried out in air by pulsed laser photolysis of flowing mixtures containing Cl<sub>2</sub> and suitable precursors. Reagent concentrations were measured by optical absorption (Cl<sub>2</sub>) and by metered gas flows. Conditions were chosen to maintain [HO<sub>2</sub>] >> [RO<sub>2</sub>], which simplifies the analysis. The specificity and sensitivity of LIF were exploited to measure the OH yields. The LIF response was calibrated before and after each yield measurement by adding metered amounts of nitric oxide, which produces known [OH] in the reaction HO<sub>2</sub> + NO. Numerical simulations using a detailed chemical mechanism were used in experiment design and analysis.

This excellent paper confirms the important finding that OH is produced in reactions of HO<sub>2</sub> with some RO<sub>2</sub> radicals.

#### Technical Corrections

Abstract: should state that the branching ratio  $\alpha_1$  was measured at 298 K.

p. 7115, paragraph starting on line 16: the new paper published in Nature [Lilieveld et al., Nature 452, 737-740 (2008)] should be cited here

p. 7117, line 24: please state the purity of N<sub>2</sub>, O<sub>2</sub>, and the Cl<sub>2</sub>/He mixture. Perhaps it's implicit in "Messer 5.0", but unless one knows the code (does 5.0 mean "five nines" or 0.99999 pure?), the purity is not knowable without a search.

p. 7121 (bottom) and 7122 (top): Although the mechanism in Appendix A is quite detailed, the time-dependent OH signal is mostly controlled by only a small number of elementary reactions. It would be good to add a sentence to this effect.

p. 7124ff and figure captions: it would help to satisfy my curiosity if the peak [OH] was given either in the text or (preferably) in each figure caption.

p. 7125, lines 5 and 12, and Table 1: was the temperature varied? What, specifically

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

is the temperature? Please give T in the table heading.

Fig. 4: here, the OH signal dips around 0.5 ms, rises to a local maximum around 1 ms, and then decays monotonically. Is this behavior reproducible? Could it be an indication of a more complex mechanism or of an experimental artifact? Noise? This point should be addressed in the text, if only to be dismissed.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7111, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

