

***Interactive comment on* “Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation” by Y. J. Liu et al.**

Anonymous Referee #2

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Liu et al. describe recent experiments designed to probe the photochemistry of isoprene oxidation by OH under NO starved conditions. They suggest small yields of methacrolein (MACR) and methyl vinyl ketone (MVK) are produced from the reaction of isoprene hydroxy peroxy radicals with HO₂.

This is an important study with implications for atmospheric analytical chemistry. The authors show that signals in PTRMS that have traditionally associated with MACR and MVK can be produced via ionization of the isoprene hydroxy hydroperoxides. The experiments performed – including those using model hydroxy hydroperoxides – are of high quality. This will require a critical re-evaluation of other measurements us-

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ing PTRMS and conclusions derived from such measurements (such as estimates of MVK/MACR fluxes).

The main criticism I have of the study is that the estimate of the uncertainty in the yields of MVK/MACR from the RO₂ + HO₂ reactions is unrealistically small. Unfortunately, sensitivity of the instrumentation used was not capable of constraining the [NO] to better than 70 ppt and as such a significant fraction of the RO₂ loss may have resulted from NO chemistry. Attempts to estimate this fraction using models is problematic given the uncertainty in rates and products of the associated reactions (e.g. HO₂ + RO₂). In the absence of a measurement of NO, do the authors have any information on the production of alkyl nitrates? These can provide a rather direct estimate of the NO chemistry. As it stands, I suggest that authors perform a critical sensitivity analysis of the possible yield of MVK and MACR from NO in their chamber and report the yield of MVK/MACR from the HO₂ channel with the appropriate limits (e.g. 15 ± 0.7% recycling will probably be 12 ± 3-5%; this also assumes 0 recycling in the delta channels which may or may not be true).

Finally, I believe that recycling in RO₂ + HO₂ chemistry has also been reported by Wallington and co-workers in halogen substituted 'Rs'.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 33323, 2012.

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