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Interactive comment on “Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-oxidation: on the paradoxical role of dissolved molecular oxygen” by P. Renard et al.

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General comments

This paper describes a series of experiments designed to investigate the reactions of OH radicals with methyl vinyl ketone (MVK) in aqueous solutions with varying oxygen concentrations. The goal is to elucidate mechanisms by which high molecular weight compounds are generated within atmospheric aerosols.

Hydroxyl radicals were produced in bulk aqueous solution by photolysis of hydrogen

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peroxide; MVK was added and its concentration followed by uv-vis spectroscopy, after removal of excess H₂O₂ with catalase. Products were assessed using mass spectroscopy and NMR. Specifically, oligomers derived from MVK radical polymerizations were identified.

Oxygen concentrations were manipulated by changes in temperature to change the saturation concentration or by purging with argon. O₂ was assumed (or measured?) to become supersaturated with the decomposition of H₂O₂.

Overall, the work is well done and well documented. Certainly the authors have demonstrated that photoinitiated polymerization of MVK is feasible in oxygenated aqueous solution.

The relevance to atmospheric processes should be clarified. The concentrations of MVK used (0.2-20 mM) are extraordinarily high (which explains how NMR analysis was possible!). As has been pointed out in other comments, oxygen is likely to be near equilibrium in atmospheric aqueous phases. However, I presume that at higher altitudes O₂ partial pressures are lower, and so aqueous levels would be proportionally lower as well. I am not expert enough in this area to assess the effects of altitude or the balance between decreasing pressure and the competing fact that lower T increases O₂ solubility.

While the experimental MVK concentrations are very high relative to atmospheric conditions, the time scales are very short. To what degree would very long reaction times at lower MVK levels give similar outcomes? Can some of the intermediates (e.g. alkyl peroxides) in Fig. 10 act as reservoirs for continuing radical chain reactions even at much lower initial reactant concentrations? Fig 8b is interesting, showing that in at least one aspect the effect of initial low O₂ concentrations does not affect the products obtained after 50 minutes.

Specific comments

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p. 2918, line 16: I'm surprised to see a Pyrex flask used. Pyrex light transmission drops off below about 330 nm where the H₂O₂ absorbance band starts. Obviously this worked, since the H₂O₂ was effectively photolyzed.

p. 2929, line 8 (and elsewhere). I assume "external" refers to the beta-carbon and "internal" means the alpha-C. I would assume that beta-addition would be greatly favored because resonance with the carbonyl gives it a stronger positive character.

p. 2918, lines 8-9. I assume "photostationary conditions" refers to H₂O and HO concentrations. Correct? The H₂O loss rate should be quite sensitive to pH (rxn R4, S1), so its concentration is expected to decrease rapidly as the pH drops from 6 to 3 (Fig 5).

p. 2919, line 13: Was O₂ also measured with the Consort analyzer that was used for pH? Not clear.

p. 2928, line 21: The formation of an oligomer containing a terminal vinyl group means there is an opportunity for additional radical reactions. Is that important for atmospheric timescales?

Technical corrections

p. 2915, line 10: under atmospheric relevant conditions. → under atmospherically relevant conditions.

p 2916, line 16: HULIS is not defined before use.

p. 2917, line 1: mechanisms

p. 2917, line 20: "more intense (less than an order of magnitude)" is confusing.

p. 2920, line 6: "to evidence" -> "to demonstrate"

p. 2920, line 12: organics -> organic

p. 2951, Fig. 8: MVK concentration not indicated.

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p. 2938: Check format for Benson and Krause citation.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2913, 2013.

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