

Interactive comment on “Kinetic measurements on the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes, ketones and organic acids in aqueous solution” by L. Schöne and H. Herrmann

Anonymous Referee #2

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Understanding multiphase processes in the troposphere is clearly key to a thorough understanding of the fate of organic matter. This manuscript addresses part of this problem through a series of kinetic measurements of the reactivity of hydrogen peroxide and ozone towards small atmospherically relevant aldehydes i.e., ketones and organic acids in aqueous solution. The scientific motivation is sound as non-radical oxidants like hydrogen peroxide and ozone may contribute to the degradation and conversion of this kind of compounds.

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The experiments were performed using UV/Vis spectroscopy (dual-beam spectrophotometer and Stopped Flow technique) and a capillary electrophoresis system applying pseudo-first order kinetics of glyoxal, methylglyoxal, glycolaldehyde, glyoxylic, pyruvic and glycolic acids as well as methacrolein (MACR) and methyl vinyl ketone (MVK) towards H₂O₂ and ozone.

Despite the fact that the measurements indicate rather small rate constants, this chemistry is discussed to play a significant role as H₂O₂ and ozone may be abundant. Overall I do find this paper very interesting and recommend its publication after some changes to strengthen its content.

The experimental section starts with underlying the need for spectroscopic information about at least for one reactant. But the manuscript does give any spectroscopic information. Maybe it would be useful to add

Also, there is no indication on how the ozone solutions were prepared and stored. This could be important as some ozone generators do produced NO_x and once transferred into an aqueous solution this may alter its ionic strength and therefore the measured kinetics. Therefore, adding some practical information here would be useful to the reader.

Also, I did miss some information about the mixing times in both approaches (dual-beam spectrophotometer and Stopped Flow technique). Please add this information just to make sure that the mixing times was indeed very short compared to the observed lifetimes. This may be also important in assessing the linearity of the observed decays.

Concerning the H₂O₂ measurements, how was the catalase acting? How fast was its reaction? Did this introduce some uncertainties in the reported reaction advancement times?

To what are the reported uncertainties referring to? Just the uncertainties in the fitted

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slopes or do they convey more parameters?

After reading the result section, I'm still confused about the possible reaction mechanism, especially for aldehydes for which two distinct reaction schemes are provided. Is there a way from your data to rationalize this into a single reaction mechanism? In chemistry, the terminology turnover has a precise definition and refers to catalytic processes (including enzymology). Therefore, its use in the context of this paper may be misleading or leading to confusion. Best would be to avoid its use or if not to give a precise definition. The units given to it corresponds rather to a rate constant. . . So some clarification would be welcome.

Specific comments

Title: Wouldn't "Kinetic measurements of. . ." be nicer?

The engineering notation should be avoided in the figures.

Abstract: what is meant by "substance group"? Also referencing papers in an abstract is unusual. . .

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25537, 2013.