

Interactive comment on “Emissions and photochemistry of oxygenated VOCs in urban plumes in the Northeastern United States” by R. Sommariva et al.

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We would like to thank Referee 2 for reviewing our paper and apologize that it took so long to reply to the reviews. We will prepare a final version of the manuscript taking into account the comments. Our response to the comments:

Page 12374, line 6: the main criterion for an RO isomerisation reaction to be possible is generally the availability of a hydrogen atom to allow a 1,5 H atom shift to occur. This is not possible, for example, in the case of 3-pentoxy, whereas it is in the case of 1-butoxy. Therefore the statement of the need for a carbon chain of at least 5 atoms is incorrect, and needs to be modified.

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Page 12374, line 9: the carbonyls formed in R2, R4, R5 and R6 are all aldehydes as written, as the reactions use the example of a primary peroxy radical. It is therefore incorrect to say they can be either aldehydes or ketones, without some additional qualifying information.

The reviewer is correct and we will correct and clarify these points in the text of the final version of the paper.

Page 12381, line 21: It is indicated that the alkene ozonolysis routes can only form acetic acid on day 1 when, presumably, the routes via CH₃C(O)O₂ are inoperative owing to NO_x level. The fact that essentially no formation is simulated on day 1 therefore suggests that the alkene ozonolysis routes are not important. Can this be clarified? Is there sufficient water in the simulation to scavenge the Criegees, if formed significantly?

The reaction of the Criegee with water yields acetic acid. The point here is that alkenes are almost completely consumed by the end of the first day. The main loss process for alkenes is the reaction with OH, which is much faster than the reaction with O₃. By the time ozonolysis becomes important, the concentration of alkenes is too low to produce significant amounts of Criegees and, hence, acetic acid. This is why the "Criegee route" is not an important source of acetic acid and most of the acetic acid is produced by the reactivity of CH₃C(O)O₂, under the conditions used in the model. This point will be made clearer in the final version of the paper.

Page 12381, line 24: It is not clear which rate coefficient(s) for the formation of acetic acid are being referred to here. Do they relate to ozone/alkene reactions or reactions of Criegees with H₂O? In the latter case, a difference in rate coefficient may not have any effect if the process is dominant.

What is discussed in this paragraph is actually the formation of acetic acid from CH₃C(O)O₂ and not from the Criegees. The text will be clarified.

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Page 12381, line 26: Information accessed from the IUPAC website in 2003 does not necessarily represent the "latest recommendation", and probably cannot be obtained anymore. Is it possible to tie the actual information used to the recommendations presented in one of the series of IUPAC special issue volumes, published in ACP since 2004? (also page 12376, line 14)

The expression "latest recommendation" refers to the time when the model was assembled and used. This will be amended in the final version of the paper. All the editions of the IUPAC evaluation since 1999 are available on the website (http://www.iupac-kinetic.ch.cam.ac.uk/past_summary.html).

Page 12383, line 6: it should be clarified that the alpha-pinene-derived RO radicals decompose to yield acetone.

Page 12383, line 8: acetone formation from IPECO results from decomposition, rather than reaction with O₂.

Thanks to the reviewer for pointing out these mistakes. We will correct and clarify the text in the final paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12371, 2008.

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