

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

Anonymous Referee #2

Received and published: 31 July 2008

This paper presents an analysis of the formation mechanisms for a number of small oxygenated VOCs (acetone, MEK, acetaldehyde, acetic acid and methanol) in urban plumes, using box model simulations in which the Master Chemical Mechanism (MCM) was used to describe the detailed chemistry of about 60 emitted organic compounds. The results are compared with observations of the oxygenates made during sampling of urban plumes from an aircraft in a pseudo-Lagrangian experiment. A main focus of the analysis is to establish those emitted VOCs which represent the most important precursors to each of the oxygenates as a function of time during the processing of the plume over a period of several days. With the exception of identifying routes to acetic acid formation, the analysis provides a strong endorsement of the representation of the

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



chemistry in the MCM, and a good demonstration of how it can be used to examine detailed atmospheric organic chemical processes. The paper is acceptable to proceed to full publication in ACP, although the authors should consider the following minor points.

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.

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.

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 $\text{CH}_3\text{C}(\text{O})\text{O}_2$ 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?

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 H_2O ? In the latter case, a difference in rate coefficient may not have any effect if the process is dominant.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



2004? (also page 12376, line 14)

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.

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

ACPD

8, S5439–S5441, 2008

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

S5441

