Atmos. Chem. Phys. Discuss., 6, S3914–S3916, 2006
www.atmos-chem-phys-discuss.net/6/S3914/2006/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Formation of secondary organic aerosol and oligomers from the ozonolysis of enol ethers” *by* A. Sadezky et al.

A. Sadezky et al.

Received and published: 18 October 2006

The referee remarks that the sentence in the abstract (page 5630, line 10 to 13) cited below might lead to a confusion of the reader: “The main stable gas-phase reaction product is the respective alkyl formate ROC(O)H, formed with yields of 60 to 80 %, implying that similar yields of the corresponding Criegee Intermediates (CI) CH_2O_2 for the AVE and CH_3CHO_2 for EPE are generated.” The referee argues that the yield of the Criegee Intermediate should not vary for different types of alkenes, as it is the direct decomposition product of the primary ozonide in its excited form, citing Finlayson-Pitts and Pitts (2000) as a reference. The referee then asks if these yields eventually refer to the stabilized form of the Criegee Intermediates CH_2O_2 and CH_3CHO_2. We agree that this sentence is not clear. In the cited passage, we do not refer to the stabilized Criegee Intermediate, but indeed to its excited form. In order to prevent misunderstandings in the future, we will add the mention “excited” before the term “Criegee Intermediates (CI)” in the above cited sentence.

We want to emphasize that the initial gas-phase mechanism of the reaction of enol ethers with ozone is explained in detail on pages 5633 to 5635 (section 3.1) and illustrated on Figure 1. As is the case for the ozonolysis reactions of any unsymmetric alkene, the primary ozonide formed from the addition of an ozone molecule to the alkene double bond can decompose via two different pathways, leading to the formation of two different carbonyl compounds and two different corresponding excited Criegee Intermediates. The given yields of 60 to 80 % for the excited Criegee Intermediates CH_2O_2 (AVE) and CH_3CHO_2 (EPE) originate from the measured branching ratio of the major decomposition pathway of the primary ozonide formed during the first step of enol ether ozonolysis, as is clearly explained on pages 5633 to 5635 (section 3.1). The alkoxy-CI ($ROCHO_2$) formed by the minor decomposition pathway of the primary ozonide accounts for the remaining yields of 20 to 40 % of excited Criegee Intermediates, and the yields of the excited Criegee Intermediates formed from both pathways of course always sum up to 100 %. We furthermore mention on page 5634 (lines 18 to 19) of our publication that the yields of the stabilized Criegee Intermediates CH_2O_2 (AVE) and CH_3CHO_2 (EPE) are estimated to be nearly 20 to 40 % per reacted enol ether (Sadezky, 2005). We consider our explanations on pages 5633 to 5635 and in Figure 1 (section 3.1) sufficiently clear and detailed for an unambiguous understanding of these issues.

Concerning the gas-phase ozonolysis mechanisms of alkenes, a more detailed reference than Finlayson-Pitts and Pitts (2000) is given by the book of Calvert et al. (2000), where branching ratios of primary ozonide decomposition and yields of stabilized CI for a large variety of alkenes, alongside with mechanistic explanations, can be found.

The referee furthermore recommends to use the expression “room temperature” instead of “atmospheric temperature” in the abstract (page 5630, line 6) in order to refer to a temperature of 296 K. We already use the expression “room temperature” in the experimental part (page 5632, line 6) and will do so in the abstract as well.

Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J. and Yarwood, G.: The mechanisms of atmospheric oxidation of the alkenes, Oxford University Press, 2000.

Finlayson-Pitts, B. and Pitts, J. N.: Chemistry of the upper and lower atmosphere. Academic Press, 2000.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5629, 2006.