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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* “Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds” *by* S. M. Saunders et al.

**S. M. Saunders et al.**

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We are grateful to both referees for their generally very supportive comments on the paper, and concerning the Master Chemical Mechanism itself. Neither referee has any substantial criticisms of the paper, but each raises a small number of comments and queries which have either been reflected in minor amendments to the paper, or are replied to below.

Referee 1, comment 2: Degradation of VOCs to CO2 and water

With reference to the statement "This process is continued until the chemistry either yields CO2, or until an organic product or radical is generated for which the subsequent

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chemistry is already represented in the mechanism" (page 1852, lines 14-16), the referee points out that the complete gas phase degradation of VOCs to CO2 and water in the atmosphere may be intercepted by physical deposition or gas-aerosol transfer of some intermediate products. The authors are in complete agreement with the refereeŠs view. However, the present paper and, in particular, the section where this statement appears, is describing the methodology used to construct gas phase degradation mechanisms for VOCs. We therefore feel that the discussion of deposition and aerosol formation processes at this point would impair the clarity and purpose of the section. To emphasise that gas phase chemistry alone is being discussed, the first sentence of the section has been altered to read ŚThe protocol, outlined in section 4, is designed to allow the construction of comprehensive, consistent gas phase degradation schemes for a variety of non-aromatic VOCŠ.

Referee 1, comments 3 and 4: Formation of Criegee intermediates from ozone-alkene reactions, and their reactions with water

The referee suggests that formation of dialkyl-substituted Criegee intermediates should be favoured over monoalkyl-substituted Criegee intermediates in alkene systems where both can be generated from the reaction with ozone. At present, this is only the case for a- and b-pinene. In all other cases the two possible channels are currently assumed to compete equally, although revision of the representation of these reactions is being considered in ongoing work. It should be stressed, however, that the majority of alkene systems considered in the mechanism are adequately represented by the current assumption of a 50:50 split.

The referee also queries the representation of the reactions of stabilised Criegee intermediates with water. The treatment of all the removal reactions (including the reaction with water) is fully described in the previous protocol (Jenkin et al., 1997), and is therefore not repeated in the present paper. Recent developments in the understanding of the structural dependence of the reactions with water (e.g. as reported within the EUROTRAC-2 CMD community) will be considered in future work.

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Referee 1, comment 6: Mechanism validation using chamber data

The referee makes a general comment about the need to test/validate the MCM (as far as possible) using chamber datasets for VOC-NOX photo-oxidation experiments. The authors are in agreement with this view. As stated in the paper, no extensive testing of the mechanism as a whole using environmental chamber data has been carried out. However the process has commenced (as demonstrated for a-pinene in the present paper, and for toluene by Wagner et al., 2002), and more widespread testing of the mechanism is one of the main objectives of ongoing work.

Referee 2: Comparison of MCM v3 with previous versions

The referee comments first on the presented validation of the isoprene and a-pinene schemes within MCM v3, and queries why comparisons with the performance of previous versions of the mechanisms are not presented. The previous protocol (Jenkin et al., 1997) did not cover the degradation of a-pinene, such that a comparison with a previously reported methodology is not possible for this VOC. Although isoprene was treated previously, the field data used for the validation exercise (Williams et al., 1997; Lee et al., 1998) were not available at the time. This is therefore the first opportunity to present the ability of the MCM isoprene chemistry (in any form) to recreate the field observations. Although comparison with a previous version would be possible in this case, the major updates in the chemistry (as shown in Table 3) will only influence the product distribution at much lower levels of NOX than those characteristic of the field data being used for the validation, such that a comparison would not be instructive.

The referee also suggests that additional critical comments are required about the MCM v3 POCP values and how they differ from those calculated with previous versions of the mechanism. The authors disagree on this point. The discussion as it stands in section 6.3 first deals with the general trends in POCP values. VOC classes are then identified for which the new POCP values differ notably from those reported previously, and the differences are explained in terms of mechanistic changes. Finally, POCP values for three species (a-pinene, b-pinene and 2,3-dimethyl-2-butene) for which previous values are unavailable are reported, and these are discussed in terms of POCP values calculated for alkenes in general. The authors feel that the presented material is fully adequate in terms of length and content, and that no additional discussion is warranted.

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