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Atmospheric
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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.

Anonymous Referee #1

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This article provides an overview of the updated version of the Master Chemical Mechanism, and as such is a valuable addition to the literature. Full use is made of the literature data concerning the kinetics, products and mechanism of the atmospheric reactions of volatile organic compounds (VOCs), except for aromatic hydrocarbons whose atmospheric chemistry is dealt with in the companion article (part B). This article relies heavily on the earlier Jenkin et al. (1997) publication for the details of much of the VOC chemistry dealt with, and in some places this leads to a need to refer back to this earlier publication. I have a few relatively minor comments concerning this article, as follows:

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(1) Page 1949, line 9. The authors should point out which VOC oxidation processes are not sunlight initiated (obviously photolysis, reaction with OH radicals, reaction with NO3 radicals and reaction with O3 are all directly or indirectly photo-initiated). (2) Page 1852, line 14. Not all VOCs are going to be degraded to CO2 and water; certain reaction products will undergo wet and/or dry deposition and may nucleate or partition onto/into existing particles (and therefore lead to secondary organic aerosol formation). (3) Page 1855, lines 23 and 24. For alkenes of structure R1R2C=CHR3, why not assume that formation of the dialkyl-substituted Criegee intermediate dominates over formation of the monoalkyl-substituted Criegee intermediate (for example, a 60:40 split as used for the -pinene reaction)? (4) Page 1867, line 15. The authors should state what the products of the reactions of stabilized Criegee intermediates with water vapor are assumed to be; a hydroxyhydroperoxide, an acid plus H2O, or a carbonyl plus H2O2, and how this depends on the structure of the Criegee intermediate. (5) Table 1. Papagni et al. (2000) did not study any branched aldehydes, and hence footnote f needs revision. (6) A general comment. While this mechanism is based on literature kinetic and product data for those reactions for which experimental data are available, and uses literature data for analogous reactions for those reactions for which experimental data are not available, there must be large portions of the mechanism which are little more than educated guesswork. However, very few comparisons of this mechanism against the fairly large database of chamber irradiations of VOC-NOx-air mixtures carried out specifically for chemical mechanism testing seems to have been done. While there are significant problems associated with chambers when studying ozone formation from VOC-NOx systems, a comparison between mechanism predictions and chamber experimental data (taking into account the various chamber effects) would surely allow presently unknown (or poorly known) portions of the mechanism to be better formulated and/or parameterized. This would be important for those portions of the mechanism with NOx and radical sink or source reactions which significantly impact ozone production.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1847, 2002.

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