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Interactive comment on "Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction" *by* Michael E. Jenkin et al.

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This manuscript, the next in a series describing protocols for the automatic generation of chemical mechanisms, addresses the reactions of organic peroxy radicals. Methods are given for the calculation of both overall rate constants and product branching ratios.

The manuscript is detailed, and addresses all or most of the possible reaction partners for RO2 in the atmosphere. This is a lot to cover, and the manuscript is at times a little scant, but in general does a good job at giving enough information to follow what the

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Discussion paper

authors are trying to say.

I have one relatively minor technical comment, plus a general observation about alkyl nitrate yields, following on from Luc Vereecken's comment.

Page 3, line 18. The first carbon atom in this RO2 radical seems to be missing some bonds. I suspect it is meant to be the oxo dihydroperoxy radical, so C(O)(OOH)CH2... etc

Further thoughts on the temperature dependence of alkyl nitrate yields.

In their 1987 paper, Atkinson et al. [1] parameterized the nitrate yield as a function of temperature and pressure, leading to a pressure dependent term, Yo(298)*[M] multiplied by a temperature dependence (T/300)^mo with mo = -2.99, and Yo(300) = Aexp(n), where n is the number of carbon atoms. The high pressure yield in this formulation had a temperature coefficient of -4.69.

In 1989, Carter and Atkinson [2] instead parameterized the ratio ka/kb, and found the best fit with mo = 0, and m(inf) = -8.0. So all the temperature dependence was in the high pressure limit, which leverages the whole curve down to low pressure.

Arey et al. (2001) [3] adopted this latter formulation to extrapolate their room temperature values to other temperatures.

In our 2012 review paper (Orlando and Tyndall, 2012) [4] we attempted to combine the low pressure and temperature dependent terms, using Yo(298)[M](T/298). This is of course erroneous, since if mo=0 the temperature dependence vanishes (other than that implicit in [M]).

It appears that Jenkin et al. (main manuscript Page 4, line 16; SI Page 2) copied our incorrect version in their current manuscript. It is possible that Carter, Atkinson and Arey have updated their fit at some point to include a (T/298) term. However, we cannot remember having seen this anywhere (although we are even older than Dr. Vereecken, and we may have forgotten it).

We apologize for introducing this error into the literature. Note that the formula given in Calvert et al. (2009) “Mechanisms of Atmospheric Oxidation of the Alkanes” is correct, while that in Calvert et al. (2015) “The Mechanisms of Reactions Influencing Atmospheric Ozone” is not.

[1] R. Atkinson, S. M. Aschmann, and A. M. Winer, J. Atmos. Chem., 5 (1987), 91. [2] W. P. L. Carter and R. Atkinson, J. Atmos. Chem., 8 (1989), 165. [3] J. Arey, S. M. Aschmann, E. S. C. Kwok, and R. Atkinson, J. Phys. Chem., A 105 (2001), 1020. [4] J. J. Orlando and G. S. Tyndall, Chem. Soc. Rev., 41 (2012) 6294.

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