Archibald et al. focus on the sensitivity of HOx to a series of recently proposed mechanisms. A simplified mechanism is derived and implemented in a chemical transport model and the global impacts of such mechanistic changes are assessed. The authors conclude that the mechanism proposed by Peeters et al. could resolve the model/measurement inconsistency at low NOx.

In the present form and despite an interesting review of our present understanding of the isoprene photooxidation under low NOx, this study clearly lacks comparisons with fields or laboratory data to support its conclusion. This is crucial since there are many ways to "fix" OH in global models. The many studies which have investigated this topic prior to this work seem to suggest that a purely chemical "fix" may bring OH into closer agreement with the measurement but would result in inconsistencies with other VOC measurements (including isoprene) [1, 11, 6]. This in turn suggests other processes (such as dynamics) have to be accounted for in order to properly interpret field measurement. Surprisingly, this issue is not mentioned in this study.

Without a comparison with experimental data, the insights provided by this study into the isoprene - low NOx problem are not sufficient to warrant publication in ACP. However, I would strongly encourage the authors to incorporate their mechanism into a more complex box model to test it against results from field campaigns [11, 6].

Comments

p5865	add reference to [13]
p5870	the section on high NOx reaction of isoprene peroxy radical should be removed or made substantially shorter since no change in the standard MCM chemistry is made.
p5870	I would not say there is a consensus on isoprene nitrates yield. Recent lab studies seem to suggest the yield could be relatively high [12, 7, 10] though a recent study using a chemical transport model concluded the yield of isoprene nitrates was likely small[4]. Pinho's reference is not the most appropriate (besides it is not found in the reference list).
p5873	How was the rate of (R13a) estimated ?
p5874	I do not understand why the authors chose to drive their models with varying emissions of NO and isoprene. This greatly complicates the comparisons of the different chemistries since after two days the chemistry hasn't reached steady state (especially since there is no deposition in the model). At the same time, it misses (as noted by the authors) a lot of important processes to properly model boundary layer conditions (which makes me wonder how robust is the comparison with the study of Karl et al.). As many previous studies suggested deposition and chemical segregation can greatly affect

the resulting OH. In particular, deposition of ISOPOOH has been suggested to be very fast [5] and the deposition of MVK and MACR substantially underestimated[11]. This would affect the conclusions of the authors which are looking for a purely chemical "fix". Reduction of the effective reaction rate between ISOP and OH should also be considered (but would require a more complex model).

p5874 Wouldn't the epoxide mechanism also apply to ISOPBOOH ?

p5875 The specific conclusion that chemical mechanisms (or chemical transport models) are unable to capture OH concentration under low NOx was reached by multiple investigations prior to the authors' work (Archibald 2009). This should be properly reflected in the text.

p5878 I do not think the epoxide chemistry [8] is equivalent to the mechanism depicted in Fig. 4. ISOPBOOH reaction with OH has been shown not to yield a dihydroxydihydroperoxide as suggested by the authors. The mechanism shown in Fig 4 results in the loss of two HOx in the formation of dihydroxydihydroperoxide while the formation of IEPOX is HOx neutral. This is a pretty significant difference. Furthermore the chemistry of the epoxide is likely significantly different from the dihydroxydihydroperoxide.

p5881 The authors state that half of the OH increase is related to NO, which makes me wonder if the model is properly set up to adequately compare the different mechanism (see also comment on p5874). Shouldn't the authors use a constant value of NOy instead (from field values maybe) letting the model partition between the different members of NOy [2]. That would make the comparisons between the mechanisms more consistent. This also suggests that similar conclusions could be reached if the consumption of NOx in the model was reduced. What would be the effect of a reduction of the isopn yield to 4% for instance, change in their deposition or oxidation rate or even changes in the night time chemistry ....

p5882 The rate of HPCH4CHO photolysis should be given in the text, especially given its uncertainty. Since this is by far the largest source of OH in the mechanism, I think it crucially demands some experimental validation.

p5883 What is the yield of HPCH4CHO with the slow Peeters' mechanism ? What is the yield of MVK and MACR (normal and slow Peeters' chemistry) ? What is the yield of the isoprene hydroxyperoxide (normal and slow Peeters' chemistry) ? How does it compare with previous studies ?

p5883 Shouldn't the radical originating from HPCH4CHO photolysis isomerize to make an acid ? This would considerably reduce the hydroxyacetone yield. Under low NOx condition, one would also expect reaction with HO2 to dominate which would reduce the yield of hydroxyacetone.

p5892 Given the very large uncertainties in the chemistry presented in this study and the lack of new evidence supporting this scheme, the authors should be a lot more cautious with the reported increase of OH (two significant digits !). Another illustration of this very large uncertainty is the recent study of Ghosh et al. [3] which suggests that the branching ratio between the E and Z isomer is 1:1. This is at odds with the theoretical study of Peeters et al. [9]. How would it affect the authors' conclusions ?

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