

Interactive comment on “Parameterisation and impact of aerosol uptake of HO₂ on a global tropospheric model” by H. L. Macintyre and M. J. Evans

Anonymous Referee #2

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This manuscript describes the development and application of a parameterisation for the HO₂ reaction probability on tropospheric aerosol particles to be used in global 3-D chemical transport models. The reaction of HO₂ on or in aerosol particles has the potential to be an important sink of HO_x radicals with implication for tropospheric oxidizing capacity. However, it remains a highly uncertain and relatively poorly constrained process in terms of laboratory, field, and modeling studies. For that reason, a paper such as this can be of scientific importance to the field.

The authors utilize the available laboratory measurements of HO₂ reactive uptake to various surfaces to fit an analytical expression for the reaction probability that depends

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upon aerosol "type", relative humidity, and temperature. They then implement this parameterisation into GEOS-Chem, a 3D chemical transport model that has been used in the past to assess the impacts of HO₂ reactive uptake to aerosol particles, and compare the results between three other options for treatment of the reaction probability.

Broad Comments

In principal, I am OK with this approach, however in this particular circumstance I am concerned about the utility of the results obtained and their comparison with previous work for the following reasons. First, given (1) the very large uncertainty in the HO₂ reaction mechanism, (2) the large divergence in measured reaction probabilities over a very limited range of atmospheric conditions, (3) large uncertainties about the actual composition, pH, and phase state of tropospheric aerosols, the value of a parameterisation based on a very small number of highly idealized laboratory systems is highly questionable. The authors need to justify such a parameterisation in light of the above issues. More on the details of this issue follow below. My second concern is that this new parameterisation results in different reaction probabilities but not different impacts compared to the Thornton 2008 parameterisation that the authors also used for comparison. See for example Tables 2 and 3. And yet, even though the impacts of the two parameterisations are essentially identical relative to a situation where the reaction probability is set to a constant value, the authors seem to focus on the differences in the reaction probabilities and do not even mention as far as I can tell how similar the two parameterisations are in terms of impacts. Ultimately, isn't the interest in the effect of the parameterisation on other atmospheric constituents? A revised version should focus on the similarities between the two parameterisations and the reasons for the similarities even though the reaction probabilities are different. More on this issue also follows below.

Detailed Comments

1. The authors conclude their parameterisation is likely a "lower limit", however, that is

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only true for the small ranges that have been probed in the laboratory, and even then I would argue it is only strictly true that all laboratory measurements lead to reaction probabilities biased low. For example, using high HO₂ concentrations can potentially bias the loss rate high due to self-reaction.

2. Would it be possible to show the actual data used to make the parameterisation? At the moment I wouldn't call what is described in the manuscript a "review" of laboratory data.

3. A direct comparison of reaction probabilities from the two parameterisations is not all that instructive because what is actually of interest is the heterogeneous reaction rate, which is a function primarily of the reaction probability, particle size, and particle surface area concentration. Given the non-linear dependence of the heterogeneous reaction rate on reaction probability that arises due to the gas-phase diffusion limitation, a much higher reaction probability doesn't necessarily translate into a much higher heterogeneous loss rate. However, the authors do not mention this aspect in the text and instead only highlight the differences in reaction probability. This issue is at least partly the explanation for why, even though reaction probabilities between the two parameterisations differ, the actual impacts do not. Thus, a figure that compares the heterogeneous reaction rate would be more informative as a direct comparison. A second reason for the lack of sensitivity between the two formulations is that the heterogeneous reaction rate just isn't all that important as a HO_x sink in the regions where the reaction probabilities differ the most.

4. Pg 16318, line 9. Aren't the laboratory measurements lower limits (as mentioned earlier) due to strong diffusion limitations in the experiments? I would think the Thornton 2008 parameterisation, if it depends upon aqueous phase chemistry, would depend upon pH and thus for a truly consistent comparison the pH of sulfuric acid droplets (if that is truly a correct assumption about upper tropospheric aerosol) would have to be used.

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