Atmos. Chem. Phys. Discuss., 12, C9861–C9863, 2012
www.atmos-chem-phys-discuss.net/12/C9861/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on “Oxidation of SO_2 by stabilized Criegee Intermediate (sCI) radicals as a crucial source for atmospheric sulphuric acid concentrations” *by* M. Boy et al.

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Received and published: 27 November 2012

The authors should be applauded for their research on an emerging topic of sCI radical chemistry. To better inform interested readers about the impact of the sCI radical chemistry on sulfuric acid, I recommend the authors to consider the following suggestions:

(1) The impacts of the sCI chemistry on sulfuric acid depend on the rate constant of the sCI + SO2 reaction as well as sCI + H2O reaction. Hatakeyama and Akimoto (1994) reported that the rate constant for the sCI + H2O reaction vary widely (2.0x10-19 to 1.0x10-15). The reported rate constants for the sCI + SO2 reaction also vary substan-

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tially (Welz et al., 2012 reported 3.9x10-11, Mauldin et al., 2012 reported 6.0x10-13, previously reported values are much lower). Mauldin et al. (2012) did not report any rate constant for the sCI + H2O reaction. We conducted simulations using a box model and found that the sCI chemistry only enhances sulfuric acid when a lower rate constant for sCI + H2O reaction is used. We used the rate constant reported by Welz et al. (2012) for the sCI + SO2 reaction. Here, the authors have not stated the rate constant that they used for the sCI +H2O reaction; I suggest that it be explicitly reported in the article.

(2) The authors are perhaps using the lower limit of the reported rate constant for the reaction of sCI + H2O. Hatakeyama and Akimoto (1994) suggested an upper limit of 1.0x10-15, Welz et al. (2012) reported an upper limit of 4.0x10-15, Leather et al. (12, 469-479, 20120, ACP) reported an upper limit of 1.0x10-12. I suggest the authors also report the results of their model using the upper value of the rate constant reported in the literature. This will provide a lower and an upper range of the impacts of the sCI chemistry on sulfuric acid and the readers will be better informed of the impact of the chemistry on sulfuric acid.

(3) The authors report that the use of the rate constant for the reaction of sCI + SO2 reported by Welz et al. (2012) overestimates the sulfuric acid concentrations by 100%. Again, the results depend not only on the sCI + SO2 reaction but also on the sCI + H2O reaction. If the authors use the rate constant reported by Welz et al, 2012 for the reaction of sCI + SO2 and the upper limit of the reported rate constant for reaction of sCI + H2O, model will not over-estimate the sulfuric acid predictions by 100%. On the other hand, if the authors use the rate constant reported by Mauldin et al. (2012) for the reaction of sCI + SO2 and the upper limit of the reported rate constant for reaction of sCI + H2O, the model predicted sulfuric acid will be substantially under-estimated.

(4) The authors suggest that the new oxidation mechanism is crucial in regional and global models. We recently implemented it in a regional model and found that the impact depends on the selected rate constants for sCI + SO2 and sCI + H2O (Sar-

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war et al., 2012, potential impacts of two SO_2 oxidation pathways on regional sulfate concentrations: aqueous-phase oxidation by NO_2 and gas-phase oxidation by Stabilized Criegee Intermediates, accepted for publication by the Atmospheric Environment). When we use the rate constant reported by Welz et al. (2012) for SCI + SO_2 and a value of $2.4x10^{-15}$ (lower than the reported upper limit) for sCI + H_2O, the model does not enhance sulfuric acid. When we lower the rate constant of SCI + H_2O to $1.0x10^{-16}$, the model enhances sulfuric acid. Since the reported rate constants for both reactions vary substantially, it will be instructive to the interested readers if the authors provide recommendation on the rate constants that should be used in such models.

(5) The regional and global models do not constraint OH concentrations by observed OH values. In this study, the authors have constrained their box model with measured OH concentrations. I suggest the authors also report their box model results without constraining OH concentrations.

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