**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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The authors make an interesting analysis of SCI as a potential oxidant for SO2, combining field observations with a model analysis to quantify the expected enhancement of H2SO4 formation. We have recently published a paper (Vereecken, Harder, Novelli, PCCP 14, 14682-14695, 2012; referred to as VHN below) that may shed some light on some aspects of this analysis; that paper might not have been available yet to Boy et al. when submitting their current paper.

Key parameters for the reaction of SCI + SO2 are its rate coefficient, and the (effective) yield of SO3 or, indirectly, H2SO4. Boy et al. propose (p. 27696) that the rate coeffi-

cients derived experimentally by Welz et al, and later Percival et al. (CH3CHOO + SO2, presented at the Int. Symp. Gas Kinet. 2012) are not applicable to the atmosphere as they were obtained at lower pressure. This assertion, however, is incompatible with the potential energy surface as examined in 4 theory-based papers (Aplincourt and Ruiz-Lopez 2000, Jiang et al. 2010, Kurten et al. 2011, VHN 2012); this PES shows a barrierless addition reaction with a deep energy well, followed by several exit transition states well below the energy of the reactants. Such reactions typically have very little redissociation to the reactants at room temperature, and hence a total rate coefficient that is nearly independent of pressure. If anything, a higher pressure should lead to an increased rate coefficient, as already indicated by Welz et al. Pressure dependence of k(T) is therefore unlikely to be the reason for the difference between the experimentally measured SCI+SO2 reaction rate (Welz et al., ~10-11 cm3 s-1), and the experimental observations (Mauldin et al, ~10-13 cm3 s-1). On the other hand, as discussed and quantified by VHN, the product distribution (never quantified experimentally) is expected to be sensitive to pressure. At atmospheric pressure, it was found that only a few percent of the SCI+SO2 adduct form SO3 directly for large SCI, with the remainder mostly forming a cyclic compound. A yield of only a few percent of SO3 would lead to an effective rate coefficient for SO3 formation two orders below the overall rate coefficient, compatible with Welz et al. versus Mauldin et al. This is only a tentative explanation, as the ultimate fate of the cyclic compound is as yet undetermined.

A second point touched by VHN is the difficulty at this time to estimate the steady state concentrations of SCI in the atmosphere. The sources of SCI are ill characterized, particularly their most effective sources such as the sesquiterpenes (fast reaction with O3, high stabilization yield). Likewise, the sinks are barely known: the unimolecular decay rate of SCI is uncertain by many orders of magnitude, the rate coefficients of its bimolecular reactions are uncertain by similar magnitudes, and the concentrations of many of the coreactants (e.g. oxygenates) are also not accurately determined. While these uncertainties are acknowledged explicitly by Boy et al., and variations on the SCI+SO2 rate coefficient were incorporated in the analysis, it would be instructive

to perform a more complete error analysis, by also examining the modeled H2SO4 formation using a different set of SCI rate coefficients. An example set could be the rate coefficients proposed by VHN, estimated based on the available theoretical data as recently reviewed by Vereecken and Francisco (Chem. Soc. Rev. 2012), and found in some cases to be quite different from what is used in the MCM. In a similar vein, it might be worthwhile to explicitly consider the very large differences in reactivity/lifetime/atmospheric fate between different SCI, as highlighted by VHN, particularly with respect to their reaction with water.