

Oxidation of SO₂ by stabilized Criegee Intermediate (sCI) radicals as a crucial source for atmospheric sulphuric acid concentrations

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Anonymous Review

In this paper the authors present direct impact of new kinetic measurements of the reaction of C.I.s with SO₂. The reaction rate constants are employed in a simple model to quantify the impact of faster CI rates of reaction on the H₂SO₄ budgets. However, the estimation on the importance of the CI-SO₂ reaction and their modelling work may be inappropriately extrapolated.

1. The paper assumes that SO₃ is the product of the reaction of C.I. + SO₂. What actual experimental evidence is there for this hypothesis? In essence their work is an extrapolation of the indirect methodology of Cox and Penkett (*Nature* **230**, 321-322, 1971) It has been pointed out by the interactive comment there is very little detail given of the model set up and much more information is needed. If the authors have assumed a 100% SO₃ formation this needs to be stated and more importantly the experimental evidence (or otherwise) that they use to support their hypothesis.

2. The authors suggest that the **direct** kinetic measurements of Welz et al. are too fast. They suggest that their modeling results and observations imply a much slower rate coefficient for the reaction of CI with SO₂. However, a rate constant of 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ is supported by both experimental and theoretical work. Welz et al., reported a direct measurement for the reaction of CH₂OO with SO₂. The theoretical results of Kurtén et al. (*J. Phys. Chem. A*, **2011**, *115* (31), 8669–8681) show that the SO₂ reaction with acetone oxide, which has no alpha-hydrogen, has a barrierless entrance channel and a low-lying transition state for SO₃ + carbonyl formation, similar to that for CH₂OO + SO₂. Jiang et al. (*J. Phys. Chem. A*, **2010**, *114*, 12452–12461) theoretically characterized CH₂OO + SO₂ and the Criegee + SO₂ reactions for the CI's from limonene ozonolysis. In a similar vein to Kurtén et al, they do not report barriers on the entrance channel for either reaction. In light of these findings, it would suggest that the rate coefficient with CI with SO₂ would be faster than the 10⁻¹³ cm³ molecule⁻¹ s⁻¹ implied in the manuscript. Indeed, in more recent work Vreecken et al., (PCCP, *14*, 14682-14695, 2012) have also reported a theoretical rate coefficient of the order of 10⁻¹¹ which has been further supported by recent experimental work (Carlsson et al., PCCP, *14*, 15637-15640, 2012). A much more balanced view of the reported rate coefficients needs to be reported, indeed, specifically it should be addressed why their data is different from direct measurements, indirect measurements and theoretical work.

3. The impact of the decomposition rate of the CI will have a large impact on the order of magnitude that can be used to fit the field data. Again little information is given, for instance if a larger decomposition rate was used the rate coefficient for CI with SO₂ would have to be increased for the observational data. Indeed it has been shown that the decomposition rate can vary from 0.3 – 250 s⁻¹ (J. D. Fenske, A. S. Hasson, A. W. Ho, S. E. Paulson, *J. Phys. Chem. A* *104*, 9921, 2000). Given that the decomposition rate can vary by orders of magnitude this would imply that the rate coefficient for CI + SO₂ could be

varied by orders of magnitude to fit the observational data. A discussion of this needs to be included in the manuscript and more importantly a quantification of the fit as a function of chosen Cl + SO₂ rate coefficient for each scenario provided in a table, i.e. a sensitivity study needs to be carried out.

4. As pointed out by the open comment the reaction of Cl will also have a large impact on the impact of Cl + SO₂. Again a summary of the sensitivity of the retrieved fit as a function of Cl + H₂O is needed. Indeed, Angalada et al., (PCCP, 13, 13034-13045) using CCSD(T), CASSCF and CASPT2 *ab initio* methods in conjunction with transition state theory suggest that syn conformer of the Cl reacts fast than the anti conformer, how has this been taken into account? Regardless, a quantification of the fit as a function of chosen Cl + H₂O rate coefficient for each scenario provided in a table, i.e. a sensitivity study needs to be carried out.

5. What is the impact of the pressure dependence on the rate coefficient? In particular, Vreecken et al., (PCCP, 14, 14682-14695, 2012) have suggest that the product of the reaction of SO₂ + Cl at higher pressures would not be SO₃, however it could be a sulfur bearing secondary ozonide. What would be the impact of this? How was this taken into account in the model and again a quantification of the fit as a function of chosen Cl + SO₂ branching ratio for each scenario is required.

6. The paper states that that rate coefficient reported by Welz can not be applied to the atmosphere as they were in the low pressure regime and therefore are not applicable to tropospheric conditions. Under what circumstances is it not applicable to tropospheric conditions? If the reaction is pressure independent then the low pressure rate coefficient is directly relevant to atmospheric conditions. If the reaction is pressure dependent then the rate coefficient is a lower limit, if the reaction is pressure dependent but has reached its high pressure limit by 4 Torr then the rate coefficient is directly relevant to tropospheric conditions, but the products may change with pressure. In all cases, the rate coefficient is an important guide to tropospheric conditions.

7. In the paper it is stated that if the reaction with Cl intermediates are all orders of magnitude faster the amount Cl intermediate available for reaction with SO₂ will decrease significantly, however this statement does not seem to make sense. The steady state concentration is given by the ratio of the total production rate / total loss rate. Given that the total loss rate $\sim k(\text{decomposition}) + k_{\text{water}}[\text{H}_2\text{O}] + k_{\text{SO}_2}[\text{SO}_2] + k_x[\text{X}]$ etc., where X is another reactant. If it is assumed that the $k(\text{decomposition})$ is 200 s⁻¹ (Fenske et al., J. Phys. Chem. A 104, 9921, 2000) this means that any other species must be ~ 1 ppm if its rate coefficient is $\sim 1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for example to have an impact of steady state [Cl], so apart from water, the effect on [Cl] by any other reactant is tiny.