

Interactive comment on “Mechanism of UV-light induced SO₂ oxidation to H₂SO₄” by A. Sorokin

Anonymous Referee #1

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General comments:

This manuscript is one of several recent attempts to answer the so-called “sulfuric acid nucleation mystery”, i.e. the observation that sulfuric acid formed in situ via SO₂ oxidation seems to nucleate much better than the corresponding amount of sulfuric acid taken from a liquid solution. These explanation attempts can be divided into three categories: reinterpretation of experimental observations (including, but not limited to, experimental error), participation of other compounds (either sulfur-containing or not) than H₂SO₄ and H₂O in the nucleation process, and “alternative” (i.e. not involving the SO₂ + OH reaction) formation routes of H₂SO₄. This manuscript falls into the third category.

The mystery itself has very recently been answered (M. Sipilä et al., in press, 2010), and the true explanation seems to lie in the first category. As the author of the present

C9543

manuscript could not have been aware of this at the time of writing, this should not be taken a criticism of his work. The reaction mechanisms proposed in this manuscript are interesting, and may possibly be atmospherically relevant, even though they are not necessarily needed to explain the laboratory results. The manuscript is a valuable contribution to the rapidly growing body of knowledge on the topic of sulfuric acid formation in the atmosphere, and should be published in ACP after some (mainly technical) revisions.

Specific comments:

-The manuscript is logically laid out and fairly easy to read, though some of the phrasing is very odd. There are a number of spelling and grammar errors (see the technical corrections below for some examples). Some paragraphs are also exceedingly long, and should be split into two or more parts. None of these issues seriously affect the clarity and legibility of the text, so they are not major problems, but the author might want to have the manuscript proofread prior to final publication.

-It is slightly unclear what, if any, new experiments, simulations or calculations have been made in this work. If the manuscript just contains data analysis drawing on existing data (which has not been combined before), this is fine - several such papers have indeed been published on the very same issue – but this should be made more clear.

-Several enthalpy values are cited in the text, usually with some (often fairly old) references, sometimes without any references at all. It would be helpful to the reader if some brief mention were made of the source of these values: are they direct experiments, extrapolations from some experimental values, computational results, or what?

-Reaction scheme 1. The HOSO₂ + O₂ reaction has been proposed (supported by computational, though as yet only little experimental, evidence) to proceed via a HSO₅ (“HOSO₂O₂”) intermediate. As this species has been the focus of several other attempts to explain the “sulfuric acid nucleation mystery” (see above) this detail could at least be mentioned. Also, the SO₃ + H₂O reaction is known to be catalyzed by another

C9544

water molecule, this ought to be mentioned (or shown in the reaction equation).

-In reaction scheme R2, where does the H_2O_2 come from? In the atmosphere there is of course some H_2O_2 present, but what is its proposed source in the laboratory experiments being discussed? This should be mentioned.

-What is the source of the enthalpy values given for reactions R3 and R4?

-On page 24417 (lines 13-14) the author claims that the reaction rate of vibrationally ($v > 2$) and electronically excited O_2 with SO_2 (Reaction R6) should be smaller than $3 \times 10^{-10} \text{ cm}^3/\text{s}$, and then goes on to use this limiting value in the calculations. It is certainly true that the rate must be equal to or smaller than the value given, as it corresponds more or less to the collision rate. However, since the rate of the $v = 0-2$ reaction is six orders of magnitude slower, it seems quite a leap of faith to use the collision rate as an estimate of the reaction rate! (There is probably a non-zero activation energy even in the case of a vibrationally excited reactant. Also, the reaction might not be spin-allowed, see below.) I understand that this value is intended to be an upper limit (and this does become obvious later on in the discussion), but this should be made a lot more clear from the start. For example, the sentence (line 14-17) "Hence, the production rate" . . . certainly needs to be modified.

-On page 24417, line 22, the author contrasts the SO_3 formation mechanism involving excited O_2 with the "neutral chemistry oxidation route involving OH radicals". The description of the "standard mechanism" is correct, but the phrasing used here may be slightly misleading to non-expert readers as also the excited- O_2 route proposed here is "neutral", i.e. no ions are involved. Thus, the words "neutral chemistry" might be removed to prevent misunderstandings.

-On page 24418, the author states that most excited oxygen atoms are removed by quenching in collision with air molecules. Next, he states that "the remaining atoms rapidly transfer their energy to O_2 ". Isn't this pretty much the same thing, since energy transfer from $\text{O}(^1\text{D})$ to O_2 is quenching (though this might depend on the definition), and

C9545

O_2 is the second-most abundant air molecule? This is just a technical detail, but it could cause some confusion. Maybe "air molecules" could be replaced by " N_2 molecules", if that is what the author really means (as indicated by reaction scheme R8)? Also, some fraction of $\text{O}(^1\text{D})$ react with other species, e.g. with water to give OH (this is the main source of the OH radicals in the experiments!), so the phrase "The remaining atoms" might need some modifying, e.g. to "Most of the remaining atoms".

-What is the source of the enthalpy values given for the last two lines in reaction scheme R8? What is the justification for assuming that these reactions occur at the collision rate? If this is (again, as above) intended only as a maximum limit, this should be more clearly stated. The conclusion that the reaction of SO_2 with the highly (singlet-sigma, $^1\Sigma$) excited oxygen molecules could produce as much SO_3 as the "standard" $\text{SO}_2 + \text{OH}$ route is based on the assumption that the reaction proceeds at the collision rate, i.e. that the activation energy for the reaction is zero. Without any supporting experimental or computational evidence this seems a little far-fetched, as the $\text{O}=\text{O}$ double bond still has to be broken (and even the singlet-sigma minimum of O_2 is still bound by a couple of eV with respect to the free oxygen atoms).

-In reactions R6 and R8 (second-to-last line), an oxygen atom is formed. Presumably, the enthalpies are computed assuming that the O atom is in its ground (triplet) state. This should be indicated in the reaction equations.

-If the oxygen atoms formed in R6 and R8 (see above) are indeed in the triplet state, this raises the question of whether the reaction of singlet O_2 with SO_2 to give SO_3 and triplet O are spin-allowed. If SO_2 and SO_3 are in their (singlet) ground states, it seems to me that the reactions should be spin-forbidden. If this is the case, the reactions are likely to be very slow, in complete contrast to the assumption that they proceed at almost the collision rate. This issue must be addressed.

Technical corrections:

-Page 24412, Line 11, "The sulfur presents...", very odd phrasing, probably not gram-

C9546

matically correct, please rephrase.

-Page 24412, Line 24, "estimated in somewhere indirectly", should probably read "estimated somewhat indirectly".

-Page 24413, Line 14, "is of about few" should probably read "is around a few" or "is about a few".

-Page 24413, Reaction scheme 1, lines 4, 5 and 6: "=" should be replaced by arrows

-Page 24414, line 6 "asses" should read "assess".

-Page 24415, line 6 "Also, it is enegetically possible the chemical quenching [...]" should read "Also, the chemical quenching [...] is energetically possible".

-Page 24415, last line, "are forming" should read "are formed".

-Page 24416, line 13, "reduced" should read "removed".

-Page 24416, line 15, "can result from", odd phrasing, please rephrase (shouldn't this just read "is"?).

-Page 24416, line 26, what do the subscripts "ET" in the quenching rate constants stand for?

-Page 24417, line 1, "steady" should read "steady-state".

-Page 24417, line 3, "at" should read "in".

-Page 24417, line 6, "in dependence" should read "depending on".

-Page 24417, line 7, "low concentration limit of" should read "lower limit for the concentration of".

-Page 24417, line 10, "In result" should read "As a result".

-Page 24417, line 18-19, "The formed via Reactions (R5-R6) steady-state GSA concentration" should read "The steady-state GSA concentration, formed via Reactions

C9547

(R5-R6)",

-Page 24418, line 2, "removing" should read "removed".

-Page 24418, line 13, what does "FR" stand for?

-Page 24418, line 14, "are rapidly forming", should probably read "are rapidly formed", or perhaps "are rapidly established".

-Page 24419, line 5, "Two reactions, involving SO₂," should read "The two reactions involving SO₂".

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24411, 2009.