Atmos. Chem. Phys. Discuss., 9, C10547–C10550, 2010
www.atmos-chem-phys-discuss.net/9/C10547/2010/
© Author(s) 2010. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mechanism of UV-light induced SO_2 oxidation to H_2SO_4" *by* A. Sorokin

A. Sorokin

andrey.sorokin@mpi-hd.mpg.de

Received and published: 5 February 2010

We appreciate the constructive and very helpful comments of the reviewer #1 which help to improve this manuscript (MS).

The main: Based on comments by both Referees we suggest a slight changing in the title of the MS according to

"One conceivable mechanism of UV-light induced SO2 Oxidation to H2SO4"

as it reflects some a hypothetical character of the paper.

Our replies to the comments are given below.

1. ". . .some of the phrasing is odd and some paragraphs are also exceedingly long"

Reply: We agree to the opinion by Referee 1. In the revised MS we try to correct the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

text with such paragraphs with accounting also for “Technical corrections” by Referee.

2. “. . . It is slightly unclear what, if any, new experiments, simulations or calculations were made in this work.”

Reply: Reviewer is correct that the method used to get our results is unclear. In fact, our results are based on simple calculations using existing data for known physical phenomena – the chemistry of excited molecules. An appropriate sentence is added in the revised MS.

3. “. . . Some enthalpy values are cited without or fairly old references . . .”

Reply: The most of “old references” were taken from the NIST Chemistry Reference Data Base and we didn’t find new results. We agree that this is a weak place of the paper, but can’t improve it for the moment. In the revised MS we have tried to give more information or at least to mention that an uncertainty of thermochemistry data and rate coefficients may introduce large errors in our estimations.

4. “Reaction scheme 1 ... H2O catalyzed effect in reaction with SO3”

Reply: The authors agree with Referee 1. We have shown the catalytic effect of the second water molecule in the reaction of SO3 with H2O. Also, we have added more discussion about the scheme 1 using the recent publications by Berndt et al. (2008), Laaksonen et al. (2008) and Salonen et al., 2009.

5. “The source of H2O2 in the laboratory experiments”

Reply: H2O2 molecules are forming in the recombination reaction of two HO2 radicals: HO2 + HO2 = H2O2 + O2 (see Seinfeld and Pandis, 1998). We have added a short explanation in the revised MS. On the other hand, some of OH radicals will disappear through the following reactions before reacting with CO, OH + OH + M = H2O2 + M (Seinfeld and Pandis, 1998).

6. “The source of the enthalpy values given for reactions R3 and R4”

ACPD

9, C10547–C10550, 2010

Reply: These values were taken from the work by Sidebottom (1972) given in the reference list of the MS. The close values are also derived using the data for formation enthalpies of reagents and reaction products from NIST Chemistry Data base. We have added the explanation in the revised MS.

7. ". . . the rate of the reaction R6"

Reply: We agree with this comment by Referee 1. Actually, the upper limit for the rate coefficient for this reaction was used here. According to remark, we have modified a first part of the paragraph (p. 24417, lines 11-17) by pointing clearly that the upper limit for the rate coefficient (reaction R6) was used in the estimation to show its maximum efficiency.

8. " page 24417 line 22, a misleading sense of the word "neutral" in this sentence"

Reply: The word "neutral" was removed out of this sentence as was suggested by Referee.

9. "page 24418 lines 2-5 – the quenching of excited oxygen atoms"

Reply: The authors agree with Referee's comment. We have modified the phrase mentioned by referee and have added the new one, that the excited oxygen atoms react also with water molecules to give OH radicals. But the main removing channel of the excited oxygen atoms is their quenching by N2 and O2 molecules (i.e. without the transfer of energy to excite the oxygen molecules).

10. "The source of enthalpy values for last two reactions in reaction scheme R8"

Reply: The enthalpy values for these reactions were calculated in a standard manner based on data for formation enthalpies for reactants and reaction products in a ground energy state and with accounting for energies of discrete electronic and vibration states of molecules (as shown in MS for R6 – p. 24416 lines 7-10).

11. Question: "the electronic state of oxygen atom formed in reactions R6 and R8"

ACPD

9, C10547–C10550, 2010

Reply: O(3P) - The respective correction has been introduced in the revised MS.

12. Question: “the possible violation of the spin selection rule in reaction mechanisms R6 and R8 and their efficiency”

Reply: That is an important remark and a good question. We have introduced in the revised MS the comment regarding this “effect”. Hence, the mechanisms R6 and R8 are only speculatively considered in the paper. The final conclusion may be possible only after the proper experimental evidence. So we suggest to change slightly the title of the paper (see above) to underline it’s rather a hypothetical character.

13. “Technical comments”

Reply: Corrected.

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

ACPD

9, C10547–C10550, 2010