Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2022-88

Anonymous Referee #2

Referee comment on "Atmospheric oxidation mechanism and kinetics of indole initiated by ☐OH and ☐Cl: a computational study" by Jingwen Xue et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-88-RC1, 2022

This manuscript presents theoretical calculations on the mechanisms and kinetics of the reaction systems initiated by the indole + OH and the indole + Cl reaction under atmospheric conditions. In particular, consecutive reactions of the produced intermediate radicals with O_2 were included, and the unimolecular reactions of the subsequent radical-O_2 adducts were studied in their competition to bimolecular reactions with NO and HO_2. Relative yields for the most important reaction channels were derived. An important finding is that the N-centered radicals produced by hydrogen abstraction from the indole nitrogen react much faster with O_2 than with NO under typical tropospheric conditions. It is concluded that the formation of carcinogenic nitrosamines appears less important for indole as for aliphatic amines (at least via this reaction pathway). The detailed theoretical characterization of several very complex reaction mechanisms with advanced quantum chemical calculations and statistical rate theory must have been really painstaking work. As the problem addressed in this paper is timely, and the methods applied appear adequate, the manuscript merits publication. However, before final acceptance, the authors could further improve the quality by considering a few minor points. They should make a bit more clear (in section 2.2) why two different software packages (MultiWell and MESMER) were used. Which one was used for which reaction, and why? Please explicitly state whether you included all the channels shown in Fig. 1(A) for OH and in Fig. 1(B) for Cl in the respective master equations. In other words, did you use a full multichannel approach coupling the entire reaction system or did you solve a corresponding number of one(few)-channel master equations? Furthermore, as far as this reviewer understands, the calculations were obviously performed for a single pressure of 1 atm. Does pressure have any effect on the relative yields in the tropospherically relevant range down to say 100 mbar? And if so, what about the energy transfer parameters (e.g. the average energy transferred per collision)? After all, how do the time-dependent results from the master equation calculations (like those illustrated in Fig. 3) translate to steady-state situations in the atmosphere. Here a brief discussion would also be useful.

Some minor technical issues are:

line 9: please insert comma after nitrosamines

line 14: please insert ‘the’ before dominant

line 21: please insert ‘that’ after demonstrate

line 34: ‘10% of total gas phase nitrogen’ – probably excluding N_2

line 60: ‘the k_{OH} value’ should be correctly termed rate constant

line 78: ‘reactions’ should better read ‘reaction’

line 123: ‘phenyl group’ should probably better read ‘the benzene ring’ or ‘the C_6 ring’

line 126: The authors should mention at this point that the numbering of the atoms is given in Fig. 1.

line 239: ‘biomolecular’ read ‘bimolecular’

line 283: please insert ‘that’ after reveal (also line 250)

line 292: If you specify author contributions then please also include Jonas Elm.

Fig. S1: Please mention the pressure in the figure caption.