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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Significant production of $ClNO_2$ and possible source of Cl_2 from N_2O_5 uptake at a suburban site in eastern China" *by* Men Xia et al.

Anonymous Referee #1

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The manuscript "Significant production of ClNO2 and possible source of Cl2 from N2O5 uptake at a suburban site in eastern China" by Xia et al. presents a set of measurements of nitryl chloride (ClNO2) and molecular chlorine (Cl2) taken near the city of Nanjing, in Eastern China, in April 2018. The authors use this dataset, and related observations, to analyze the formation of ClNO2 and Cl2 and to draw conclusions about the underlying multiphase chemical mechanism.

The paper is well written and the data are presented in a clear and concise way. The analysis and the results are sound and the authors propose some novel ideas that will certainly be of great interest to the community. I only have a few, fairly minor, com-

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Discussion paper

ments, but overall I think this paper is suitable for publication in Atmospheric Chemistry and Physics.

General Comments ————————-

In Section 3.3, the authors discuss the calculation of the yield of ClNO2, comparing the "BT" parametrization by Bertram and Thornton (2009) with a new parametrization. Looking at figure 4, I am not sure I completely agree with the author's interpretation. The new parametrization proposed in this paper does indeed agree better with the observations for yields between 0.4 and 0.6; however I would argue that the agreement is worse than the BT parametrization at higher yields (around 0.8) and only slightly better at lower yields (below 0.4). Clearly, the relationship between the various parameters is more complicated than either parametrization assume, and perhaps this suggests that there are other parameters that are not currently taken into account which play a role. In any case, I suggest that the authors revise their statements in this section (and the related parts of the conclusions and the abstract) to be more accurate.

In Section 3.4, the authors propose a mechanism for the production of Cl2 during the night. The key point of the argument is that, for the observations to be consistent with each other, g(ClNO2) must decrease and there is not really a good explanation for why that would be the case. Although I agree with this logic, there may be other parameters that influence g(ClNO2) besides Cl-, H+ and Dp. In particular organics, which are mentioned as important for g(N2O5) in the previous section may inhibit the uptake of ClNO2 as well. Likewise, RH, other aerosol components, and perhaps even temperature, may have an effect. I appreciate that it is not possible to exhaust all possible parameters but I think the authors should expand their analysis a little bit here, to make a more robust case.

The authors propose that Cl2 formation is a co-product of ClNO2 when N2O5 is hydrolized on an acidic particle. I would like to see a bit more discussion of this potential mechanism. For ClNO2 the mechanism is quite straightforward: NO2+ reacts with Cl-

to form ClNO2. For Cl2 it does not seem so obvious to me how exactly NO2+ and Cl- interact to form Cl2. If the authors have a mechanism in mind please explain or add the relevant reference(s). Otherwise, if this is simply an hypothesis, then please state so clearly.

Minor Comments ————

Section 2.1: Are there other relevant parameters (e.g., NOx) that you can use to compare the two sampling sites?

Section 2.2: Can you please add the detection limits to the text? It would also be useful to see examples of spectra for N2O5, ClNO2, Cl2 and HOCl (these could go in the Supplementary Information).

Line 187: what about NO3 photolysis?

Section 3.2: It seems to me, from figure 3, that the levels of VOC also play a role, not just O3, RH and Temperature.

Lines 416-423: What about the outflow from Nanjing, which is west of the sampling site? I would think there are industrialized areas also on that part of the country not just between Nanjing and the ocean. Are SO2 and NOx very different in the two cases shown in figure 7? Can you please add some detail.

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