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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.

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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, comments, but overall I think this paper is suitable for publication in Atmospheric Chemistry and Physics. Response: we appreciate the reviewer for the positive comments and helpful suggestions. Below is the response to each comment. The reviewers' comments are italicized followed by our responses and changes shown in blue and red, respectively. And the corrections are also marked as red color in the revised manuscript. Please note that the line numbers mentioned below refer to the original submission (line numbers in the revised version has changed). Please refer to the supplement of this author comment for better views such as font colors, subscript and so on.

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. Response: we appreciate and agree your comment on our interpretation of the performance of the new parameterization at higher yields (0.75$\sim$1). We also agree that other unconstrained factors may influence φ(ClNO2). We have revised the relevant texts as below. Revision in the main text: Line 329-330 (section 3.3): The parameterized φ(ClNO2)BT+Org better matches the observed φ(ClNO2) at low to median yields (0$\sim$0.75) and the R2 and slope values in the linear regression are closer to 1 (Fig. 4b). However, the parameterized φ(ClNO2)BT+Org is smaller than the observed φ(ClNO2) at high yields (0.75$\sim$0.9), which may be attributable to other unconstrained factors in the parameterization, e.g., mixing state and phase state issues.

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. Response: we agree with the referee that other unconstrained factors, in addition to those examined, may influence the γ(ClNO2). We have now examined the dependence of γ(ClNO2) on RH, T, and other relevant aerosol components (e.g., NO3-, SO42-, NH4+, and aerosol organics). Results show no obvious dependence of γ(ClNO2) on those parameters. We have clarified this point as follows. Revision in the main text: Line 398-400 (section 3.4.1): In our study, the Dp was derived from the ratio of wet Va to Sa by assuming volume-limited uptake (Ammann et al., 2013). We also calculated Dp assuming surface-limited uptake and obtained similar Dp values to the volume-limited approach, and no correlation with γ(ClNO2)obs was indicated. Moreover, the γ(ClNO2)obs showed no obvious relationship with other factors such as T, RH, H2O, NO3-, SO42-, NH4+, and aerosol organics (figure not shown).

The authors propose that Cl2 formation is a co-product of ClNO2 when N2O5 is hydrolyzed 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. Response: we agree it would make the contention much more convincing if we

can suggest the potential formation mechanism for Cl2 from reaction of Cl- and NO2+. Here is our proposed mechanism (see below figure). According to the hybrid orbital theory, the NO2+ ion has two non-bonded π molecular orbitals due to participation of the d orbital of the central nitrogen atom (Baird et al., 1981). When Cl- attacks one of the π molecular orbitals, ClNO2 is formed. In the same way, Cl- can attach to the other π molecular orbitals of NO2+ and form a short-lived HNO2Cl2 intermediate in presence of H+. Then, HNO2Cl2 decomposes to produce HONO and Cl2.

Revision in the main text: Line 402-404 (section 3.4.1): The mechanism is depicted in Figure 7 and goes as follows. It is known that N2O5 hydrolysis on aerosol is responsible for the production of NO2+. According to the hybrid orbital theory, the NO2+ ion has two non-bonded π molecular orbitals due to participation of the d orbital of the central nitrogen atom (Baird and Tayler, 1981). ClNO2 is formed via the nucleophilic addition of Cl- to one of the π molecular orbitals of NO2+ (Figure 7a) (Taylor, 1990; Behnke et al., 1997). In the same way, we propose a side reaction that the second Cl- can attach to the other π molecular orbital of NO2+ and form a short-lived HNO2Cl2 intermediate in presence of H+. It is proposed that the unstable HNO2Cl2 decomposes to produce Cl2 (and HONO) (Figure 7b). This mechanism can explain concurrent productions of Cl2 and ClNO2 from N2O5 hydrolysis but needs confirmation by additional laboratory and theoretical studies.

Minor Comments Section 2.1: Are there other relevant parameters (e.g., NOx) that you can use to compare the two sampling sites? Response: it is a pity that only simultaneous measurements of O3 were conducted at both 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). Response: agreed. We have added the detection limits of N2O5, ClNO2, and Cl2 in the main text, and an example of spectra in the supplementary information. Below is the revision. Revision in the main text: Line 153-154 (section 2.2): The detection limits (3σ) of N2O5, ClNO2, Cl2 were 7 pptv, 2 pptv, and 5 pptv, respectively. Revision in the SI:

Figure S3. An example of the CIMS spectra taken at 18 April 01:00 LT.

Line 187: what about NO3 photolysis? Response: thanks for the reminder of NO3 photolysis, but in the present study, we focus on the nighttime chemistry of NO3. So, the k(NO3) here is the loss rate for nighttime, and photolysis is not included.

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. Response: the role of VOCs had been included in the calculation the NO3 reactivity which is dependent on VOC levels. For example, In the plume 3, the NO3 reactivity due to VOCs decreased compared that in the plume 1. So, a larger proportion of NO3 was lost via N2O5 uptake in the plume 3, which promoted ClNO2 formation.

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. Response: 1. this is a good point. We have examined backward trajectories for the whole observation period but did not identify air masses from urban Nanjing in the west. Please see the figure below. We have added the trajectories figure in the SI. Revision in the SI:

Figure S2. Daily backward trajectories arriving at the sampling sites during the field observation period.

2. The levels of NOx and SO2 are slightly higher in marine air compared with continental air in the two cases in figure 7 (see the table below). We have added this point in the main text.

Date NOx (ppb) SO2 (ppb) Note 13-Apr 13.1±3.1 3.9±0.1 Marine air passing YRD industry 18-Apr 11.5±0.6 3.3±0.3 Continental air

Revision in the main text: Line 420-422 (section 3.4.2): The average concentrations of

SO2 (3.9±0.1ppbv) and NOx (13.1±3.1 ppbv) in the marine air masses were higher than those (NOx: 11.5±0.6 ppbv, SO2: 3.3±0.3 ppbv) in the inland air masses.

References Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, 10.5194/acp-13-8045-2013, 2013. Baird, N. C., and Taylor, K. F.: The stabilizing effect of d orbitals on the central nitrogen atom in nitrogen-oxygen molecules and ions, Chemical Physics Letters, 80, 83-86, https://doi.org/10.1016/0009-2614(81)80062-0, 1981. Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO2 from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments, Journal of Geophysical Research: Atmospheres, 102, 3795-3804, 1997. Brown, S. S., Dubé, W. P., Tham, Y. J., Zha, Q., Xue, L., Poon, S., Wang, Z., Blake, D. R., Tsui, W., and Parrish, D. D.: Nighttime chemistry at a high altitude site above Hong Kong, Journal of Geophysical Research: Atmospheres, 121, 2457-2475, 2016. Taylor, R., Electrophilic Aromatic Substitution, John Wiley, New York, 1990. Wang, Z., Wang, W., Tham, Y. J., Li, Q., Wang, H., Wen, L., Wang, X., and Wang, T.: Fast heterogeneous N2O5 uptake and ClNO2 production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain, Atmospheric Chemistry and Physics, 17, 12361-12378, 2017.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-1130/acp-2019-1130-AC1-supplement.pdf

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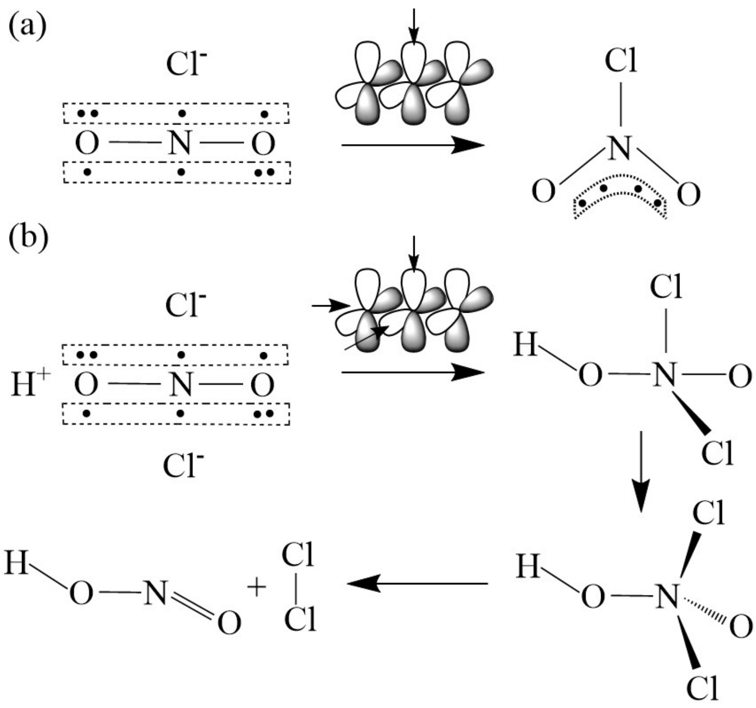

Fig. 1. Figure 7. Proposed formation mechanisms of ClNO2 and Cl2 from N2O5 uptake. (a) production of ClNO2 from NO2+ and Cl-. (b) production of Cl2 from NO2+, Cl-, and H+.

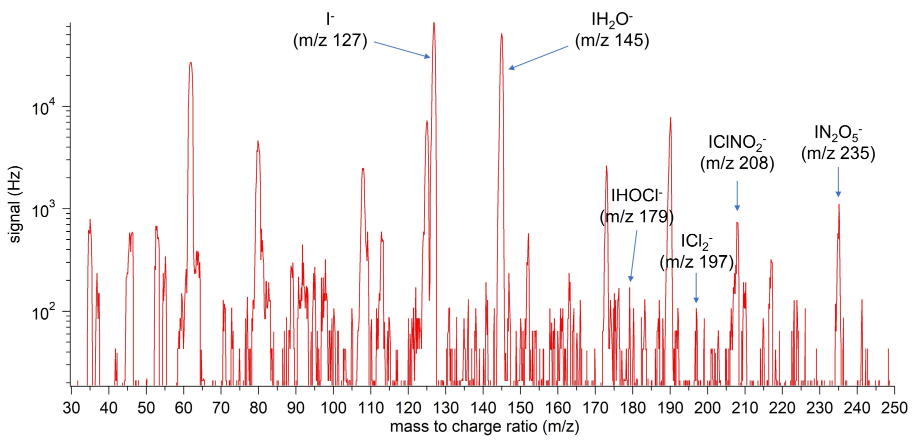

Fig. 2. Figure S3. An example of the CIMS spectra taken at 18 April 01:00 LT.

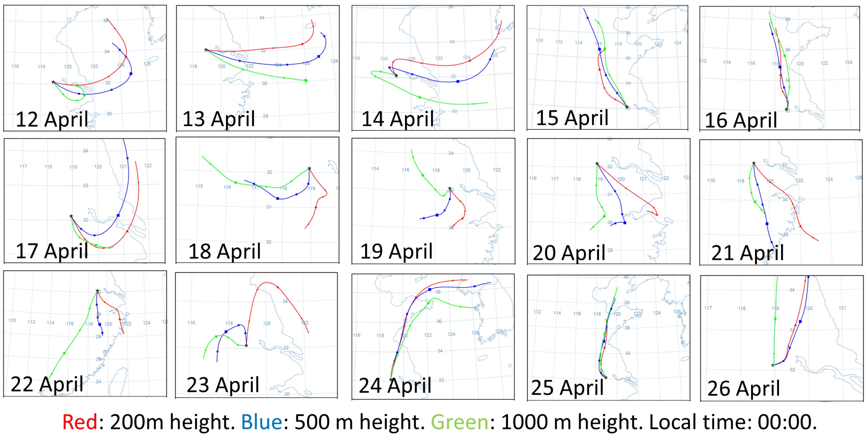

Fig. 3. Figure S2. Daily backward trajectories arriving at the sampling sites during the field observation period.