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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Production of HONO from heterogeneous uptake of NO_2 on illuminated TiO_2 aerosols measured by Photo-Fragmentation Laser Induced Fluorescence" *by* Joanna E. Dyson et al.

Anonymous Referee #1

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In this study the authors used an aerosol flow tube reactor connected to a photo-fragmentation laser induced fluorescence detection set-up to evaluate the heterogeneous chemistry of NO2 with irradiated TiO2 aerosols. The uptake coefficients of NO2 were determined for NO2 mixing ratios ranging between 34 and 400 ppb. The HONO production was determined as well at different relative humidities (RH), the highest being at 25 % RH. The performed kinetic box model suggested HONO production by heterogeneous reaction of NO2 with TiO2 aerosol surface involving two NO2 molecules, and a HONO loss which is dependent on the initial NO2 mixing ratio. Additional exper-

iments have shown that HONO is also formed upon irradiation of mixed nitrate/TiO2 aerosols in the absence of NO2. This is an interesting study following the continuation of a number of previous studies focused on this topic. The experiments are well performed and the kinetic box model was used to support the experimental results. I would suggest publication of this study in Atmospheric Chemistry and Physics as it can be of broad interest for the atmospheric chemistry community.

1) The photo-fragmentation laser induced fluorescence detection apparatus seems promising tool for online measurements of HONO in ambient air. However, the only reference about this instrument is the thesis of Boustead (2019) which is not easily accessible. I wonder if this instrument was previously used in an intercomparison campaign against other well established instruments for real time HONO measurements (e.g. DOAS, LOPAP).

2) The authors observed HONO formation upon irradiation of mixed nitrate/TiO2 aerosols and pure nitrate aerosols but they did not mention in the manuscript whether or not HONO is formed only upon irradiation of TiO2 aerosols in absence of NO2. These tests should be carried out as control experiments.

3) The authors mentioned that the aqueous solutions ready to be dispersed in the air, were obtained by dissolving 5 g of TiO2, but they did not mention the quantity of dissolved ammonium nitrate in the solution. How relevant is this amount of TiO2 dissolved in water?

4) Another very important point is that many papers related to NO2 heterogeneous chemistry on TiO2 as a HONO source are not cited and discussed. For example, Gandolfo et al (Appl. Catal. B: Environ., 2015, 166-167, 84-90; Appl. Catal. B: Environ., 2017, 209, 429-436) have shown that the disproportionation reaction of NO2, which has been also suggested as a night-time source of HONO in the atmosphere, can be photocatalytically enhanced in the presence of TiO2 which is in agreement with the statement in this study that two NO2 molecules forming HONO are required

to reproduce the experimental trend of the uptake coefficients and observed HONO concentrations. Furthermore, a similar profile of the observed dependence of HONO mixing ratios with the RH was also observed by Gandolfo et al. (2015) by detecting a maximum of HONO at 30 % RH as was measured in this study. Increase of HONO with RH on building surface containing TiO2 was also observed by Langridge et al (Atmospheric Environment 43 (2009) 5128-5131).

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