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 #2**

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The article by Dyson et al. describes a laboratory study of the efficiency of the chemical transformation of NO2 into HONO by aerosol particles, and the release of HONO from an aerosol containing TiO2 and ammonium nitrate, compounds commonly found within tropospheric aerosol. The title reflects only the first part of the study so probably should be amended.

HONO formation from NO2 is an important process for atmospheric chemistry, with implications for the free-radical budget of the troposphere. The second area, the release of HONO from nitrate-containing mineral dust aerosols, may be important if there is

TiO2 present in the mineral dust itself. This subject is therefore within the scope of ACP and will be of interest to scientists studying atmospheric free radical budgets, ozone chemistry and atmospheric oxidation lifetimes.

This paper is excellent, being an authoritative quantification of the HONO produced from aerosols (HONO being determined by photolysis of HONO and measurement of resulting OH concentration). It is clearly written and of a very high scientific quality. An aerosol flow-tube is used for the study, with supporting measurements of aerosol size distribution. The manuscript combines an extensive set of flow-tube measurements to determine the efficiency of NO2 to HONO conversion, defined as gamma(NO2-HONO) across a range of relative humidity and NO2 mixing ratios. The measurements are performed at room temperature and pressure. HONO production from TiO2-containing aerosols is quantified as a function of NO2 mixing ratio and relative humidity over the range 12-36%, with HONO production reaching a maximum near 30% RH, and afterwards declining. Observed HONO mixing ratios increase with increasing NO2 mixing ratio up to 50 ppb before declining to a constant value above approx 100 ppb which corresponds to a decreasing HONO → NO2 reactive uptake coefficient.

The measurements are discussed in the context of a box model employing three distinct mechanisms and are shown to be reproduced well by the mechanisms, adding further insight. The box model is described well and the manuscript shows the depth of physical chemistry expertise available in this leading group, and provides a valuable review of the chemistry involved which is relevant to the atmosphere.

The study of HONO release from TiO2-containing nitrate aerosols is interesting, but not treated at quite the same depth as the uptake onto TiO2 aerosols. An experiment involving single-component NH4NO3 aerosol was performed at 50% RH, while a second involving (presumably internally mixed) nitrate/TiO2 aerosols was performed at 20% RH. The relative humidity used in this study is on the low side for the boundary layer, particularly the marine boundary layer discussed in this manuscript, and the effect of humidity.

In fact, the only issue I have with the manuscript is the application of the laboratory results to the atmospheric cases mentioned. The authors note the dependence of the HONO production on RH, and even adjust experimental conditions to allow for this. The discussion of the atmospheric implications doesn't discuss the RH effect in much detail, which is a pity, because it may be an important factor, particularly in the May/June case of Beijing, although it would appear not to alter the conclusions of section 4.1, and in the (likely) high relative humidity marine boundary layer in Cape Verde. I would like to see this considered in the revised MS.

Minor points:

Figure 2: according to equation 8, the a plot of k vs SA should pass through the origin, but the plotted data do not appear to. Why is this? Can the authors comment?

L206: what is the time to establish laminar flow? How precisely is the overall interaction time between $NO_2$ and the aerosol surface area known?

L472 and Table1 - the use of a first order rate coefficient to describe the rate of adsorption is interesting, and merits further discussion. In model 1, the use of a constant rate coefficient for this step would imply (for constant sticking probability) a constant surface area. Was the rate coefficient R9 varied between experiments to account for variations in aerosol surface area density?

Figure 10. How was gamma ($NO_2 \rightarrow HONO$) retrieved from the box model?

Section 3.3.2 It would be useful here to identify the key kinetic parameters, that is the ones on which the uptake coefficients most sensitively depend. Given that many of the input kinetic rate coefficients used in the box model have been estimated, it may be useful to show an envelope or other indication of how the uncertainty in the input kinetic rate coefficients propagate through to the calculated uptake coefficients shown in Figure 10.

L637 I'm not clear on why 50% RH was used here when the experiments with the

mixed $TiO_2$/nitrate aerosols were performed at a lower RH.