Referee 2

We thank the referee for their helpful comments. Each comment in turn is shown below followed by our response in bold, and followed by any changes to the manuscript in red.

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.

We agree with the referee and have modified the title of the manuscript to:

"Production of HONO from NO_2 uptake on illuminated TiO_2 aerosol particles and following the illumination of mixed TiO_2/ammonium nitrate particles".

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.

As stated by the referee, the average RH in Beijing in summer is higher than used for our RH dependence which as the referee points out showed a decline in HONO production after ~ 30 % RH, although our data are limited in this region. Other studies regarding HONO production on TiO_2 aerosols (Gustafsson et al., 2006) and TiO_2 containing aerosols (Dupart et al., 2014) also showed a decrease in the uptake coefficient at higher RH. Hence, the NO_2 reactive uptake coefficient we use to calculate a production rate for HONO for the conditions in Beijing during summertime are most likely an upper limit. From Gustafsson et al., 2006, we can estimate that

the uptake coefficient could potentially decrease by as much as 90 % (for pure TiO_2) from a relative humidity of ~15 to the 80 % RH which was sometimes experienced in summertime in Beijing. We have changed the text in the manuscript as follows:

Pg 32, line 683. “The average RH in Beijing during summertime is significantly higher than the range of RH used in the TiO_2 aerosol experiments. In previous work (Gustafsson., et al, 2007), the NO_2 reactive uptake coefficient decreased for relative humidities above those studied here, and hence the HONO production calculated under the conditions in Beijing may represent an upper limit.”

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?

This is due to a background signal from HONO which is primarily from impurities in the NO_2 cylinder used for these experiments. In Figure 4, this background has not been subtracted, and so a comment will be added to the figure caption as follows:

“**Figure 4.** Pseudo-first-order rate coefficient for HONO production, *k* (open circles) as a function of aerosol surface area for $[NO_2]$=200 ppb and RH=15 ± 1 %, T = 293 ± 3 K and a photolysis time of 52 ± 2 seconds. The red line is a linear-least squared fit including 1σ confidence bands (dashed lines) weighted to both *x* and *y* errors (1σ), the gradient of which yields $\gamma NO_2 \rightarrow HONO$ = $(2.17 \pm 0.09) \times 10^{-5}$, with the uncertainty representing (1σ). The non-zero y-axis intercept is due to a background HONO signal owing to the presence of a HONO impurity in the NO_2 cylinder, and which is not subtracted . The total photon flux of the lamp (see Figure 2 for its spectral output) = $(1.63 \pm 0.09) \times 10^{16}$ photons cm^{-2} s^{-1}.”

L206: what is the time to establish laminar flow? How precisely is the overall interaction time between NO2 and the aerosol surface area known?

The distance to establish laminar flow is ~ 29 cm which corresponds to a time of 30 seconds. However, the illuminated section of the flow tube where HONO is generated is the second 50 cm of the tube closest to the HONO detection cell after the laminar flow has been established. The uncertainty in the volumetric flow rate, which is ~3% (controlled by the flow controller output) contributes most to the uncertainty in the illumination time.

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?

Unlike during the experiments, in which using different surface areas was necessary in order to determine the reactive uptake coefficient, for the modelling studies the aerosol surface area density was kept constant and the impact of changing NO_2 was explored. Hence, as only one surface area was used, the rate coefficient for the adsorption of NO_2 was kept constant across all NO_2 concentrations used in the model, and it was found that as the rate coefficient k_9 was lowered this step became the RDS leading to a drop in HONO production.

Figure 10. How was gamma (NO2→HONO) retrieved from the box model?

The model outputted the concentrations for HONO at a given illumination time for each initial value of NO_2, and γ was then calculated using equations 6 and 7 (Pg 12). However, in the model the aerosol surface area (SA) was kept at a constant value of 1.6×10^{-2} m^2m^{-3} as was used in Figure 6, in order to provide a direct comparison with experiment for the dependence of the HONO concentration on initial NO_2 concentration. In order to clarify this, we have modified the caption to Figure 10 as follows:

Figure 10. Experimental values (open circles with 1σ error bars), Model 2 (green line) and Model 3 (pink line) calculations for (a) HONO concentration after 52 s illumination and (b) NO_2 reactive uptake

coefficient, $\gamma_{NO_2 \rightarrow HONO}$, as a function of the initial NO_2 mixing ratio. The mechanisms used for these model runs included a 2:1 stoichiometric relationship between the NO_2 adsorbed on the TiO_2 aerosol surface and the HONO produced, as well as additional HONO loss reactions which are dependent on NO_2, see Table 1 for details. Models 2 and 3 use an Eley-Rideal and Langmuir-Hinshelwood mechanisms, respectively, for the formation of the NO_2 dimer on the aerosol surface. Modelled $\gamma_{NO_2 \rightarrow HONO}$ was calculated using Eq. 6 and Eq. 7 with a constant surface area of 1.6×10^{-2} m^2m^{-3} chosen to match the aerosol surface area density of $(1.6 \pm 0.8) \times 10^{-2}$ m^2m^{-3} shown in the experimental [HONO] values in (a).

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.

For models 2 and 3 the shape of the trend in HONO concentration versus NO_2 concentration depended strongly on the NO_2 dependent loss reaction, R19, whereas the shape of the trend in uptake coefficient, γ, versus NO_2 concentration depended strongly on the choice of a 2:1 stoichiometric ratio of the NO_2 molecules adsorbed to the HONO molecules produced. Without these two key processes being included, the outputs of models 2 and 3 look similar to the trends seen in Figure 9 for Model 1 (no maximum in either HONO or γ as the NO_2 concentration is increased). A third key condition was the requirement that the desorption rate coefficient, $k_{R16} = 5 \times 10^{-2}$ s^{-1}, had to be larger than the rate coefficient for the loss of HONO, 1×10^{-3} s^{-1}, but slower than the adsorption rate coefficient, k_{R9}, in order to reproduce the trend in HONO versus NO_2 seen experimentally.

Changing the values of all other kinetic parameters in the model had an effect on the absolute concentration of HONO but crucially not on the shape of the trends in HONO or the uptake coefficient versus NO_2 concentration. Changing the values of the rate coefficients for the gas phase loss reactions, R23-27, had a negligible effect on the HONO concentration, whereas changing the rate coefficients for the surface loss processes, R17-18, had more of an effect, whilst still small in comparison to changing the NO_2 dependant loss reaction, R19. Loss of NO_2 and HONO by gas phase photolysis, R20-21, also only had a small effect on the HONO concentration with the loss of gas phase HONO to the walls, R22, having a very large effect on the absolute concentration, but not on the trend of the HONO concentration or uptake coefficient with NO_2 concentration.

We performed a sensitivity analysis, during which each rate coefficient for reactions 17-27 was increased by a factor of 5 to see the effect on the [HONO] outputted for Models 2 and 3. The results are shown in the table below:

Reaction	**Description**	**Average percentage difference in HONO with an increase in *k* by a factor of 5**	
		Model 2	**Model3**
R17	Surface loss of HONO/ NO_2 independent loss reaction	-4	-5
R18	Surface loss of HONO/ NO_2 independent loss reaction	-2	-4
R19	NO_2 dependant loss reaction	-154 (% diff increased with increasing NO_2 ranging from -0.006 to -451)	-114 (% diff increased with increasing NO_2 ranging from -0.003 to -447)

R20	NO_2 gas phase photolysis	11 (% diff increased with increasing NO_2 ranging from -2.5 to 44)	12 (% diff increased with increasing NO_2 ranging from -0.93 to 53)
R21	HONO gas phase photolysis	-17	-10
R22	Gas phase HONO wall loss	-314	-270
R23	Gas phase loss of HONO	0	0
R24	Gas phase loss of NO_2	0	0
R25	Reactions of triplet oxygen / Gas phase loss of NO_2	0	0
R26	Reactions of triplet oxygen	0	0
R27	Reactions of triplet oxygen	0	0

In order to aid understanding of the key kinetics parameters, we have replaced lines 558-563 with the following text in the manuscript:

Page 27, line 558. “For models 2 and 3 the shape of the trend in HONO concentration and uptake coefficient, γ, versus NO_2 concentration depended strongly on the value of k_{R19} reaction, R19, and the choice of a 2:1 stoichiometric ratio of the NO_2 molecules adsorbed to the HONO molecules produced. Without these two key processes being included, a maximum in either the HONO concentration or γ as the NO_2 concentration is increased could not be obtained in the model. A third key condition was the requirement that the desorption rate coefficient, k_{R16}, be larger than the rate coefficient for the loss of HONO, k_{R17} and $k_{R18}=1 \times 10^{-3}$ s^{-1}, but slower than the adsorption rate coefficient, k_{R9}. Changing the values of all other kinetic parameters in the model had an effect on the absolute concentration of HONO, but crucially not on the shape of the trends in HONO or the uptake coefficient versus NO_2 concentration. Changing the values of the rate coefficients for the gas phase loss reactions, R23-27, only had a very small impact on the HONO concentration.”

L637 I’m not clear on why 50% RH was used here when the experiments with the mixed TiO2/nitrate aerosols were performed at lower RH.

Sorry, this is a typographical error. The calculations were done at the same RH as the experiment was performed at. The text of the revised manuscript has been made modified as follows:

Pg 30 ln 637. “Using the Aerosol Inorganic Model (AIM) (Clegg et al., 1998; Wexler and Clegg, 2002), the nitrate content of the aerosol at both 20 and 50% RH was calculated, in accordance with the experimental RH conditions.”