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Interactive comment on "Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR" *by* F. Rohrer et al.

F. Rohrer et al.

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Reply to editor's comment

We would like to thank the editor for his interest in our study and his very detailed comments and corrections. The concerns he raised are addressed below:

1. Presentation of parameter dependencies of photolytic source term:

The SAPHIR chamber is an outdoor chamber in which J(NO2) and temperature are clearly fixed by the ambient conditions as already mentioned in the paper. E.g., the temperature at the chamber can vary between -25 °C - +40 °C and J(NO2) can vary between 0-10ˆ-2 sˆ-1. In addition, the relative humidity can clearly change during the experiments, caused by the ambient variability of the temperature (the variability is not

constant for different days) and also by the addition of water during some experiments. We introduced a new table showing the different conditions for each of the experiments. This table includes the temperature range, the humidity range, and the maxima of J(NO2) and of the HONO source term. In addition, the heating of the chamber by irradiation is now specified in the text. The humidity range can also be extracted from Figure 4. Since all conditions change simultaneously during the experiments, a plot of S(HONO) against a single parameter like humidity or photolysis frequency without some normalization is confusing. Since we want to demonstrate that equation (E1) describes the HONO formation with high accuracy we have chosen to extract the partial dependency of S(HONO) on humidity by a normalizing procedure using equation E1 in figure 4 and the partial dependency on temperature in figure 3. In addition, this normalisation used for Figures 3 and 4 are now explained in chapter 4.2 and the unit of (S(HONO), equation (E1), is now specified. Accordingly, we think that any further figure etc. would not significantly improve the outcome of the paper. As recommended, the main difference between the experiments shown Figure 1 and 2, i.e. the use of the filter foil and the excellent agreement with the model, is now explained in section 4.1. Additionally, figures 1 and 2 now include the presentation of S(HONO) and temperature. This also allows to visualize the small effect on temperature when the chamber is exposed to illumination.

2. The effect of filtered light:

Since not only J(NO2) was varied by using a filter foil in these experiments (also: temperature, weather/clouds = variation of J(NO2) during each experiment, humidity, J(HONO)...), the excellent description of the HONO production for the very different conditions can only be demonstrated by the excellent agreement with the model calculations using equation (E1). This is done in figure 4. We highlighted the experiments of type “C” and “D” to show that experiments using CO (type “C”) and experiments using CO and the filter foil (Type “D”) are well inside the range of the other experiments. Since it was shown, that CO has no effect on the HONO production in SAPHIR (see chapter

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4.2, last paragraph), experiments with and without CO can be directly compared. Additionally, we included the S(HONO) term in figures 1 and 2 and used the same scale for the presentation so that these figures can be directly compared. To clearly show the (missing) effect of CO, we have highlighted the experiments with CO in figure 4. The reason for using the filter foil in combination with CO is that the model calculations with the target to interpret the NOx budget are more accurate because the reaction of NO2+OH is not significant under these conditions.

3. Mechanisms of the photo enhanced HONO production:

a) Exclusion of the photo enhanced NO2 reaction: Since NO2 adsorbs much weaker to surfaces like e.g. HNO3 or HONO and since our initial NO2 concentration was in the very low ppt range, a surface saturation of adsorbed NO2, i.e. monolayer adsorption can be excluded. Only for monolayer adsorption the zero order NO2 dependence, observed in our study, could be explained by any NO2 surface reactions (see also the NO2 + organics reactions mentioned in the comment from Ammann, Stemmler and George). However, since an increase of the NO2 concentration by three orders of magnitude, i.e. from a few ppt to 35 ppb (experiment type “E”), had no influence on the production of HONO in SAPHIR, surface reactions of gaseous NO2 can be clearly excluded to explain the observed photo enhanced HONO formation. This argument and the exclusion of the photolytic NO2+organic reactions (George et al., 2005) are now included in the manuscript. In addition, adsorption of HONO on the Teflon surface, formed during prior experiments by any NO2 reactions, as proposed in the comment by Ammann, Stemmler and George, can also be excluded. In this case, HONO should desorb from the walls in the dark when the humidity is increased, as observed in other chambers (e.g. Syomin and Finlayson-Pitts, 2003). This information is now also included in the manuscript.

b) Nitrate and HNO3 photolysis: In this point we agree with the editor, since the UV absorption of adsorbed HNO3 on Teflon surfaces is unknown as already mentioned in our manuscript. However, for high humidity and multilayer water adsorption (also observed

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on Teflon surfaces), the formation of nitrate was observed by FTIR spectroscopy. Since the nitrate absorption spectra is well known, our humidity dependence and especially the strong HONO formation at high humidity can be neither explained by nitrate photolysis (wavelength range using the filter foil) nor by the photolysis of adsorbed HNO3 (will not exist e.g. at 80 % r.h.). Thus we also feel very confident that this process is not of importance in the SAPHIR chamber.

c) J(NO2) correlation: This point is completely correct. We have deleted this sentence. However, we can still limit the major wavelength range to 370-420 nm for the HONO production on the walls of SAPHIR caused by the spectra features of the filter foil (most important range of the product: sigma(NO2) x quantum yield(NO2) which is linear correlated to J(NO2)).

d) exclusion of surface reactions of gaseous NO2: see point a)

e) Discussion p 13-15:

By this discussion the photolysis of nitrate/HNO3 is excluded (s. also arguments in point b). Thus we would like to leave this paragraph as it is. In addition, in the comment by Ammann, Stemmler and George even a more deeply discussion of the mechanism was recommended. In this comment hypothetical nitrogen containing organic compounds were proposed (the same which we were thinking of in our proposed reaction of HNO3 with organic compounds in the Teflon foil....), which we have now included in the manuscript.

4. Comparison with other data:

The information that the HONO formation in SAPHIR is smaller compared to other chambers is now added in the discussion section presenting some examples from the literature. But, as already mentioned, equation (E1) should not be used for the prediction of S(HONO) in other chambers, i.e. it is not applicable, as e.g. recently demonstrated for the EUPHORE chamber in a poster presentation on the Faraday discussion

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130. It should be used only for comparisons unless its applicability is explicitly justified.

5. Weakness of the study:

In this point we disagree with the editor. It is now possible to describe the HONO formation in the chamber over periods longer than one year by equation 1. This is an improvement, which was never obtained in any other chamber worldwide. Sudden changes by much more than a factor of 2 from day to day are e.g observed in the EUPHORE chamber, depending on prior experiments. This difference is caused by the very different experimental conditions in both chambers. Thus the constant background reactivity observed in SAPHIR over long periods is really the strength of this paper, although this must be checked in regular intervals, as this is certainly done in SAPHIR and as this is already recommended in the paper. In addition, in the present study we could determine the background reactivity and prove that HONO is the precursor of the background reactivity for the first time. Besides this, we could directly exclude for the first time mechanisms postulated by other groups based on indirect observations. We don't know to what degree our results are transferable to other chambers or if each chamber has its own process of background reactivity. Nevertheless, although the mechanism is still unclear (this is the weakness...), we are quite confident that our studies significantly improves the knowledge about the background reactivity in simulation chambers by showing that it is measurable, reproducible, and constant for long periods of time and by determining its major dependencies.

Special errors:

p2 Abstract, l 6: changed

l 15-16: The equation was deleted from the abstract, since otherwise to complicated at this point...

p4 l 1: changed

l 13: changed

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l 19: changed

p5 l-9: changed

p6 l 5: changed

l 20: changed

p 7 last line: changed

p8: changed

Results, l 2: changed

l 9: changed

p 9, l 5: changed

l 7: changed

l 11: changed Also Table 3: rate constants from JPL were used, see 4.2 first sentence. Now also specified in Table 3. Specific rate constants cannot easily be specified, since they depend on p, T,...

l -3: changed

p10 l 1: Recommendation not clear and highly speculative. Sentence should only demonstrate that the initial HONO is small compared to the photolytic formation. However, sentence deleted.

Equation E1: unit inserted

l -3 changed

l -2 changed

p11 l 5: changed

l 7 changed

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l 16 changed

l 17: But... exchanged by However,...

l 20: changed and normalisation explained

l 27-28: Argument expanded. The argument is important since figure 4 shows that the parameterisation is also valid for experiments type “C” and “D” with CO and with the filter foil. The chemistry is changing in experiments of type “C” (simplification of the NOx budget) and the photolysis frequencies are altered by the filter foil in type “D”.

p 12, last sentence of first paragraph: This sentence was not modified, since also photolytic NOx formation, as observed on glass surfaces, could be excluded in SAPHIR. This is of importance, since our mechanism is based on the assumption, that HONO is the only NOy source in the chamber.

2nd para, l 4-5: changed

l 8: changed

last line: changed

p13 l 9: not changed, since nitrate photolysis can be clearly excluded by the filter foil experiments (no irradiance in the spectral range of the nitrate band around 300 nm).

p15 l -4: changed

p16 l 15-16: “(see Figures 1 and 2)” added, since they clearly show this

p17 summary l 3: changed

p24 Table 1: Table deleted, and document modified accordingly

p25 Table 2: Additional table included presenting these (and additional) parameters for each of the experiments

Table 3: JPL reference now added

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Figure 3: changed

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