

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

R. Cox (Editor)

rac26@cam.ac.uk

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Editor's Report on ACP-2005-0165 (revision 1)

The revised version of the paper has addressed points made by the editor and covers some points raised by the reviewer. The revisions were, however, only minor and there are several outstanding issues of argument and presentation which need to be covered more fully, before the paper can be taken forward for publication in ACP. I suggest that the authors provide a substantially revised paper in accord with the suggestions below which are based on the reviewers comments and the interactive discussion.

Considering first the key issues raised by the referee and the authors response:

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1. Presentation of parameter dependencies of photolytic source term.

In their response, the authors correctly point out that $J(\text{NO}_2)$, RH and ambient temperature are not independently varied parameters. But in the paper, this important factor in the choice of analysis method for the kinetics is not emphasised enough - it should be spelled out more clearly in the paper. What is the 'natural variability' of temperature? (p7-8) Does it increase when the system is exposed to light? Some more specific comments on the temperature range and variability are needed. The reviewer asks that more of results should be shown. I agree with this as the results are the most valuable contribution of this study. Table 2 should at least show the maximum rates of HONO formation or max. HONO concentrations for all the experiments. Some description should be made in the text about what was observed in Figs 1 & 2, highlighting the key points. The key kinetic data presented in Figs 3 and 4 is not explained properly. Units should be given for $S(\text{HONO})$ in equation E1 and it should be explained how the rates are normalised for the plots.

2. The effect of filtered light

As the reviewer points out the relative effect of the filter foil is not evident from Figs 1 and 2 as presented. The HONO production rates should be plotted on the same scale so that they can be directly compared. Also the two experiments shown are not strictly comparable as CO was added in the second experiment shown. Experiments from type D and E need to be compared in the Figure (or at least in the Table 2) and the salient differences summarised.

3. Mechanisms of the photo enhanced HONO production

The referees' dissatisfaction with arguments concerning the wavelength and concentration dependence of the photolytic process are not fully addressed. Considering that the process clearly involves heterogeneous surface reactions, neither the kinetic dependencies on gas phase concentration (NO_2) nor on absorption regions of gas phase or aqueous species (NO_2 , NO_3^- , HNO_3) can be rigorously argued when the nature of

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the heterogeneous species is unknown. The rejection of other mechanisms derived from studies in different conditions should be more qualified in tone. There is also a problem with the $J(\text{NO}_2)$ parameter. This is the photolysis rate of NO_2 and includes the product of absorption cross section and quantum yield. NO_2 absorbs strongly at wavelengths longer than the cut off for $J(\text{NO}_2)$. On p13, it is stated that the HONO precursor adsorbs at a similar wavelength compared to NO_2 adsorption at wavelength <370 nm and exclusively >420 nm can be excluded NO_2 absorbs strongly throughout the 400-500 nm region but photolysis (in the gas phase) falls off rapidly at >400 nm due to energetic restrictions. I don't think the authors can be so confident that surface NO_2 is not involved in the HONO production. As summarised on p 15, the section where the mechanisms are discussed does not actually reach any conclusion. The discussion pp 13 - 15 should be more focussed on comparing rates in other chambers, with less emphasis on the more speculative mechanistic discussion which is inconclusive.

4. Comparison with other data

The authors have pointed out that, contrary to referees' suggestions, the photolytic rate of HONO for free radical production is less than in other chambers. Nevertheless, the examples given in their response should be presented in their paper along with remarks of the applicability of the parameterisation for other chambers.

5. One weakness in the work is the sudden and unexplained change in the fitted parameter, a , during the period of the experiments. Text about the need to periodically revise the parameter is now covered in the revised version, but it makes the generality of the conclusions less useful. This weakness needs to be highlighted.

The new version should take account of the following errors and omissions on the first revised manuscript

p2 Abstract, l 6 atmospheric, (not atmosphere). l 15-16 actual (constant) values of R_{HO} and T_0 (from Table 4) should be given in the expression for $S(\text{HONO})$ and $a_{1,2}$ should be defined.

p4 l 1 replace phrase ' , caused by conditions' by 'and,' and link to next sentence.

l 13 insert 'and on' after '2001),'

l 19 replace ' of significant importance' by 'clearly important'

p5 l -9 replace 'then' by 'than'

p6 l 5 replace 'tubing' by 'tube'

l 20 replace 'In' by 'For the'

p7 last line 'cannot' be adjusted

p8 delete last part of paragraph 1 beginning 'with several ...' (it is unclear and adds nothing).

Results section

l. 2 'overnight' is one word

l 9 change text to 'humidifier had not been operated for some time'. Also, delete following sentence commencing 'it is probably ...' (it is purely speculative and adds nothing).

p 9 l 5 move 'were' to after 'irradiation'

l 7 dominant

l 11 delete sentence beginning 'In the spectral range ...' (it has already been stated)

Also, in Table 3, RATE COEFFICIENTS USED IN THE MECHANISM SHOULD BE ENTERED IN TABLE.

l -3 delete 'and succeeding NO and NO₂ formation' (reactions R3 does not give NO and NO₂ formation directly and stoichiometrically)

p10 l 1 Photolysis of the small amounts of HONO might be the trigger for the heterogeneous reactions

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Equation E1 - insert appropriate units of S(HONO)SAPHIR,i

l -3 insert 'investigation of' before atmospheric

l -2 insert 'the' before 'processes'

p11 l 5 'particular', not 'certain'

l 7 'listed', not 'mentioned'

l 16 alkenes

l 17 delete 'But'

l 20 Text should be: 'Figure 3 shows normalised values of S(HONO) calculated using optimised parameters, as a function of 1/T(K).' [Note the normalisation procedure must also be explained in the text]. l 27-28 meaning of sentence is not very clear

Discussion section

p 12 Delete last sentence of first paragraph. The logic is unclear and the work on snow is not relevant to the discussion here.

2nd para, l 4-5 replace 'can be clearly excluded' by 'is considered unlikely'

l 8 'was' not 'were'

last line insert 'does not occur in SAPHIR', in place of 'was not observed'

p13 l 9 replace 'can be excluded' by 'does not seem likely'

p15 l -4 'advise', not 'support'

p16 l 15-16 'The calculated ... measurements'. There are no measurements shown in Fig 5 to support this statement. It should be removed.

p17 Summary l 3 'production', not 'productions'

p24 Table 1 This table is not needed. the information could easily be given in the text.

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p25 Table 2 Needs expanding to include measured [HONO] or rate in each experiment.

Table 3 Insert rate coefficients used in the model.

Figure 3 Incomplete axis number labelling on ordinate.

I am also appending to this report a comment sent directly to me but not posted on the open discussion (presumably because it was closed). It makes some useful points supporting the importance of the results but highlight the uncertainty in the mechanisms. The authors may like to take these remarks into account too.

Comment on

Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR F. Rohrer, B. Bohn, T. Brauers, D. Brüning, F.-J. Johnen, A. Wahner, J. Kleffmann By

K Stemmler and M Ammann Labor für Radio- und Umweltchemie, Paul Scherrer Institut, 5232 Villigen, Switzerland. Fax:+41 56 310 4435; Tel: +41 56 310 4049, E-mail: markus.ammann@psi.ch;konrad.stemmler@psi.ch.

C George

Laboratoire d'Application de la Chimie à l'Environnement (UCBL-CNRS) 43 boulevard du 11 Novembre 1918, F-69622 Villeurbanne, France. Fax:+33 (0)4 72 44 8114; Tel: +33 (0)4 72 43 1489, E-mail: christian.george@univ-lyon1.fr

HONO formation has been hypothesised as an important (unwanted) OH radical source in simulation chambers for a long time. This hypothesis was based on an unknown source mechanism, which could be to some wall photochemistry. During this study, this production of HONO was unequivocally identified in the SAPHIR chamber using a HONO specific instrument (i.e., the LOPAP device) under reproducible and controlled conditions at atmospheric concentrations.

It was shown that the HONO production was indeed photoenhanced. But also that

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the source strength only depends on the photonic flux, humidity and temperature. This means that the HONO photo-production is not caused by direct fast NO₂ dark reactions nor by NO_y photochemistry. Indeed, the photolysis of nitrate, recently postulated for the observed photolytic HONO formation on snow, ground, and glass surfaces, was excluded in the SAPHIR chamber.

It certainly appears that this study probably for the first time carefully characterises the source of HONO in illuminated (and non-illuminated) simulation chambers. The main outcome is a phenomenological understanding of the importance of the HONO source strength from the chamber walls based on well-constrained parameters, in the SAPHIR chamber.

However, a chemical understanding of how HONO is formed is missing and also seems impossible to be retrieved from the present data set. Here, a more in depth discussion of how it could be formed would be appropriate, as there is a significant body of literature to this part of chemistry leading to nitrite or HONO.

While there is no evidence for direct oxidation of NO to HONO other than via the gas-phase reaction with OH, the more oxidised species, NO₂ and HNO₃ could be reduced to HONO. It is well-known that apart from the disproportionation reaction of NO₂, the latter can easily undergo one-electron reduction in aqueous solution by phenoxide ions, which has been investigated for methylphenols and hydroxybenzenes (Alfassi et al., 1986, Gutzwiller et al., 2002). Several authors have also studied the kinetics of reactions of NO₂ with phenol derived biomolecules such as amino acids (e.g. glycylytyrosine, Prütz et al., 1985), as well as antioxidants such as ascorbate (Huie, 1994, Forni et al., 1986), catechins (Miao et al., 2001) and hydroxycinnamic acid derivatives (Zhan et al., 1998). Further known reactants may also be aromatic amines (Saltzman, 1954). While these reactions are aqueous phase processes, it has been shown that a similar mechanism may occur also in a non-aqueous environment when exposed to humid air, such as for solid 1,2,10-trihydroxyanthracene, where HONO has been observed as a primary product (Arens et al., 2002).

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To what degree could this chemistry occur in typical chambers experiments, or more specifically chemistry in Teflon foils is hard to judge. It was however shown that this chemistry could be efficient, even in the dark, by some modelling studies (Lahoutifard et al, 2002). As a matter of fact, from the pure absence of correlation of HONO emission with the NO₂ concentration, this chemistry cannot be excluded. The chemistry of formation of nitrite or HONO must not necessarily be linked in time with HONO emission, if for instance emission occurs from a significant reservoir of HONO built-up during past exposure of the wall to probably very different mixtures and concentrations of organics and NO_x. Such chemistry could at least explain where the nitrogen comes from, an important issue addressed by the editor in his comment.

We could imagine that this already interesting article could be improved when the authors would speculate about the chemical form which leads to the storage of nitrogen oxides in the Teflon membranes, as this material is known to be porous and to capture non negligible amounts of NO_x.

The authors showed clearly that the NO_x production is due to a reservoir of precursor substances that is likely present on the reactor walls. Some inorganic precursors as nitrate, NO₂ and probably also nitrite could be excluded by the discussed experiments. But what can be said about organic nitrogen oxides? There are some classes of organic nitrogen oxides which are known to be formed during atmospheric VOC oxidation, for example organic nitrates, nitro aromatic compounds, pernitric acids, organic nitrites. For which of them direct photolysis can be excluded due to their absorption spectra? Which NO_y species would they produce upon photolysis?

Alfassi, Z.B., Huie, R.E., and Neta, P.: Substituent effects on rates of one-electron oxidation of phenols by the radicals ClO₂, NO₂, and SO₃⁻, *J. Phys. Chem.*, 90, 4156-4158, 1986. Arens, F., Gutzwiller, L., Gaggeler, H.W., and Ammann, M.: The reaction of NO₂ with solid anthracene (1,2,10-trihydroxy-anthracene), *Physical Chemistry Chemical Physics*, 4, 3684-3690, 2002. Forni, L.G., Mora-Arellano, V.O., Packer, J.E., and Willson, R.L.: Nitrogen dioxide and related free radicals: electron-transfer reac-

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 7881, 2004.

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