

## ***Interactive comment on “Heterogeneous conversion of NO<sub>2</sub> and NO on HNO<sub>3</sub> treated soot surfaces” by J. Kleffmann and P. Wiesen***

### **Anonymous Referee #1**

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Referee Report on “Heterogeneous Conversion of NO<sub>2</sub> and NO on HNO<sub>3</sub>-treated soot surfaces” by J. Kleffmann and P. Wiesen submitted to ACPD

This paper presents an interesting case of a heterogeneous reaction that could affect the NO<sub>x</sub>/NO<sub>y</sub> balance by virtue of the potential reducing power of flame soot with respect to oxidized nitrogen such as NO<sub>2</sub> and HNO<sub>3</sub>. Proposed some years ago by several modeling groups the laboratory community is busy confirming or rejecting this reaction. The studies presented in this paper appear solid and well carried out despite their qualitative character and in line with past work presented by these authors. However, in light of recent results highlighting the complexities of the flame soot substrate it is a pity that the authors chose to base their conclusions on only one substrate, namely a commercial amorphous carbon product, rather than on fresh flame soot generated in the laboratory. A critical comparison between two types of soot substrates would have

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been more instructive. The authors cite all recent relevant work in comparison with their own work. However, I am not sure that the authors compare their experimental results with the literature on a sound basis. For instance, Aubin and Abbatt passivate their n-hexane soot for 20 to 30 minutes before recording and evaluating HNO<sub>3</sub> uptake. Choi and Leu bake their different soot substrates for a few hours at 250°C (523K) before investigation in a laminar coated-wall flow tube. Can the authors expect their results to be comparable to these two despite the seemingly excellent agreement as to the number of HNO<sub>3</sub> molecules making up a monolayer? The results of Salgado-Munoz and Rossi are in apparent contradiction to the majority of literature results on HNO<sub>3</sub>/soot interaction. However, they report the first few minutes of the HNO<sub>3</sub>/soot interaction where the products, either HONO or NO/NO<sub>2</sub>, are observable. This is such a short time interval compared to the present observation period that the authors surely would have missed this episode because the authors have chosen a bulk technique whose time resolution is in the tens of minutes according to Figures 2 and 4. How appropriate is the comparison with spark generator soot used by Kirchner et al.? This type of carbonaceous substrate has never seen any thermal oxidizing conditions (flames) such that it is inappropriate to call it soot. Therefore, I believe, the authors should give serious thought as to how and which results from the literature they compare and cite in support of their own results. They should compare what is comparable, and for the case that it is not they should draw the attention of the reader to this fact. In addition, this work could benefit from the clarification of the following questions: - Pg. 6752, line 23: What would be a typical reaction time (life time or inverse of the pseudo-first order rate constant) of a HNO<sub>3</sub> molecule with the supported carbon coating? Could the authors think of a known heterogeneous reaction that may serve as a reference? - Pg. 6754, line 21: Choi and Leu report products whose rate of formation during HNO<sub>3</sub> uptake is very low. However, they report reaction products such as NO and NO<sub>2</sub> resulting from thermal desorption/reaction runs after the uptake of HNO<sub>3</sub> has been halted. In addition, these authors stress repeatedly that they have evidence of additional N- and O-containing products on all types of soot they have investigated without identifying them. Can the

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present authors confirm the absence of any reaction products other than NO and NO<sub>2</sub>? - Pg. 6755, line 2 and regarding the data in Figure 2: What is the HNO<sub>3</sub> concentration? Are these the only data the authors have in support of HNO<sub>3</sub> reaction on soot at high HNO<sub>3</sub> concentration? - Pg. 6755 and 6756: The fact that lamp black 101 (this study) and decane soot (Salgado Munoz and Rossi) have similar yields of HONO resulting from reaction 1 does not mean that the reducing power towards HNO<sub>3</sub> (reaction 2) should also be the same, unless the authors have independent evidence for it. Do the authors think that the reducing sites for NO<sub>2</sub> and HNO<sub>3</sub> are identical (Page 6757, lines5-8)? If they think so they should clearly state it by summarizing the arguments in favor of it. - Pg. 6756, line 17: Doesn't the use of the BET surface area in the evaluation of the uptake coefficient imply a lower limit rather than an upper limit? Usually, kinetics experiments imply effective surface areas that are smaller than the measured BET surface areas. I realize that the HONO and NO<sub>2</sub> yields are upper limits, but the authors should evaluate the composite uncertainty in both counteracting parameters, surface area and yield.

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Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6747, 2004.

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