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Interactive comment on "Heterogeneous conversion of NO_2 and NO on HNO_3 treated soot surfaces" *by* J. Kleffmann and P. Wiesen

Anonymous Referee #2

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This paper reports results of an experimental study of the interaction of nitrogen oxide species with soot surface in relation with potential importance of these processes in the chemistry of the atmosphere. Interaction of HNO3 with soot was investigated in numerous previous studies. The main still open question is whether the HNO3 uptake on soot is a reactive one or this process is just a reversible HNO3 adsorption. In a few studies NO, NO2 and HONO were observed as the products of HNO3 reaction with soot. Analysis of the literature data shows that the appearance, yield and the nature of the reaction products depend on many experimental parameters: concentration of HNO3, temperature, type of soot, soot preparation (flame richness) and sampling conditions (in/out of flame). Thus, a new insight to the reaction mechanism implies additional ex-

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periments under varied experimental conditions. Unfortunately, this is not the case in the present study: only one type of soot used, experiments were carried out only at room temperature, no kinetics but only the number of molecules taken up measured. Another major comment concerns the authors analysis of the literature data. This analysis does not seem to be always exact. For example, reading the paper one has an impression that reactive uptake of HNO3 at low HNO3 concentrations was observed only in one work (Salgado & Rossi), whereas Seisel et al. using low initial concentrations of HNO3 (3’10*10 -1.0’10*12 molecule cm-3) reported that only a small part of the adsorbed HNO3 (less than 10%) was desorbed from the soot surface and HNO3 uptake was considered as irreversible on the timescale of their experiments. Kirchner et al. observed a FTIR spectra of the surface reaction products for concentration of HNO3 varied in the range from 0.054 to 2.2’10*14 molecule cm-3.

Minor comments and questions

Page 6753, line 15-16. Were the HNO3 uptake on the filter holder and the timescale of this process comparable with those on soot sample surface?

Results and Discussion, Figure 2. Figure 2 does not contain any information about kinetics of HNO3, NO and NO2 at high ($>$800 ppb) concentrations of HNO3. It seems that similar Figure however showing temporal behaviour of HNO3 and reaction products at “high” initial concentrations of HNO3 should be added.

Page 6754, line 11-15. Does it mean that the uptake coefficient of a “sticky” molecule HNO3 is unity? Kirchner et al. have observed similar kinetic behaviour for reactions of NO2 and HNO3 with spark generator soot.

Page 6755, line 1. The maximum number of active sites of 2.2’10*14 cm-2 was determined by Kirchner et al. for reaction of NO2 with soot but not for HNO3. The number of sites active toward HNO3 can significantly differ.

Page 6756, line 23-26. Concerning the speculation on the possible role of humidity, it seems that it was quite simple and easy to check (one experiment under low humidity conditions) if the different humidity in the present study and that of Salgado & Rossi is responsible for the difference in the results between these two studies.

Page 6757, Section 3.3. Was the deactivation of soot surface by NO2 formed at high HNO3 mixing ratios observed experimentally? In fact, the experiments with soot pre-treatment with high ($>$800 ppb) concentrations of HNO3 would have been interesting from the kinetic and mechanistic point of view. Another interesting experiment would have been a simultaneous introduction of HNO3 and NO2 in contact with soot sample.

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

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