

Interactive comment on “Ozone decomposition on Saharan dust: an experimental investigation” by F. Hanisch and J. N. Crowley

F. Hanisch and J. N. Crowley

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General Comment:

The current manuscript is much improved over the first version that I reviewed. The axes on graphs now make sense and plots have been lined up properly with respect to the axes. Many of the references provided in my first review indicating that this is not the first study of ozone uptake and destruction on powders and authentic dusts have been added. One section that was poorly referenced has now been removed. However, there are still some additional problems with the referencing as well as a few scientific problems that are noted below. Most importantly, the authors are using a model to take into account surface area properly and because of this there is now good agreement found between studies in different laboratories.

Reply to general comment

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In this study we have applied the pore diffusion model to correct the measured geometric uptake coefficient for internal surface. The dependence of the geometric uptake coefficient on sample mass showed that this was the appropriate way to analyse the data. Contrary to the implications of the reviewers comment above, this is not always the case, as has been documented on several occasions: F.F. Fenter, F. Caloz and M.J. Rossi, *J. Phys. Chem.* 98, 9801-9810, 1994, F.F. Fenter, F. Caloz and M.J. Rossi, *Atmos. Env.* 22, 3365-3372, 1995, P. Beichert and B.J. Finlayson-Pitts, *J. Phys. Chem.* 100, 15218-15228, 1996, F.F. Fenter, F. Caloz and M.J. Rossi, *J. Phys. Chem.* 100, 1008-1019, 1996, F. Caloz, F.F. Fenter and M.J. Rossi, *J. Phys. Chem.* 100, 7494-7501, 1996, F. Hanisch and J.N. Crowley, *J. Phys. Chem.* 105, 3096-3106, 2001, F. Hanisch and J.N. Crowley, *Phys. Chem. Chem. Phys.* 3, 2474-2482, (2001).

It is unclear what "the good agreement between the studies" refers to, and why this should be solely the result of applying a pore diffusion model. Direct comparison can only be made with the work of Michel et al., who used similar surfaces. Although "good agreement" was found at one particular ozone concentration, these authors found no dependence of the uptake coefficient on this parameter, suggesting that the results would be divergent at all other ozone concentrations (see reviewers comment below). Other studies did not use Saharan dust and qualitative comparison can be made, which is found in section 3.

Specific Comment 1

The discussion on the use of the pore diffusion model states "Keyser and co-workers have developed a model for ice surfaces (Keyser and Leu, 1991, 1993) which in principle can also be applied to granular surfaces (e.g. Timonen et al. 1994; Leu et al., 1995). This model predicts a linear dependence of the uptake coefficient on mass..." The term "in principle" suggests that this paper represents a first example where this model has been applied to granular surfaces. It is clear that there are several references missing here most notably the Underwood et al. (2000) reference. In the Underwood et al. paper (*JPCA*, Vol.104, pages 819-829, 2000), the use of the KML model in Knudsen

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cell experiments was described for the very first time. Since Underwood et. al. (2000), many if not all studies using the Knudsen cell technique for measuring heterogeneous reaction kinetics on powders are now reporting a more careful investigation of the powder thickness dependence. This is important so that the surface area can be more accurately taken into account in these studies. The discussion the authors give in this section about the model, the use of the model and characteristics of the model, e.g. a linear and plateau regime, is very close to that given in Underwood et al.(2000) and therefore that paper should be properly referenced.

Reply to specific comment 1

Early application of the pore diffusion correction in a Knudsen cell predates the study of Underwood et al. (2000) by several years (e.g. F.F. Fenter F. Caloz and M.J. Rossi, J. Phys. Chem 100, 1008-1019, 1996.) The application of the model is in any case independent of type of experiment, i.e. Knudsen reactor or flow tube. In order to avoid a long list of citations, we prefer to refer the reader to the pioneering texts of the Kaiser group rather than the numerous later applications.

Specific Comment 2

What are the error bars in the $O_2:O_3$ ratio? What are the assumptions in determining the $O_2:O_3$ ratio? This is important given that it is suggested that there is "missing" O_2 . The discussion of the deactivation/reactivation mechanism has me somewhat confused and puzzled. It is not clear what the authors are trying to say and how it relates to ozone destruction on dust in the atmosphere. Are the authors suggesting that ozone destruction is not catalytic, in contrast to what has been shown in many other studies?

Reply to Specific Comment 2

Assumptions in determining the $O_2:O_3$ ratio are discussed in detail in section 3.2.1. Error limits on this ratio, and the source of errors are already given. Our results clearly show that the presence of high ozone concentrations the conversion of O_3 to O_2 is

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not catalytic, i.e. surface is consumed. Studies of the loss of ozone on saharan dust surfaces are limited, though passivation effects have previously been documented (see section 3.3) We therefore do not agree with the reviewers implication that catalytic destruction on Saharan dust has been seen in many other studies.

Specific Comment 3

Is the deactivation of Saharan sand toward ozone destruction only important at an ozone pressure of 1 Torr? Does the mechanism for ozone uptake change at a pressure of 1 Torr compared to pressures that are six orders of magnitude lower? If so, this deactivation mechanism is a "non-issue" for the atmosphere and perhaps should be noted in a footnote instead of in the main portion of the text. In the text it states that in Hanning-Lee et al. (1996) and Michel et al. (2002), no pressure dependence on the ozone destruction rate was reported. Why do the authors think they obtained a different result in their study?

Reply to Specific Comment 3

In this study we do not use Saharan sand, but re-deposited Saharan dust which has a very distinct mineralogical composition. The fact that we see significantly less than 1.5 O₂ molecules formed per O₃ molecule lost at all partial pressures of O₃ used (including those found in the atmosphere) indicates that this is not a phenomenon unique for conditions where 1 Torr of O₃ is present. This is already discussed in section 3.3. We state that Hanning-Lee et al., and Michel et al. did not see a dependence of the initial uptake coefficient on the ozone concentration. As the same surfaces were not involved in these experiments, it is difficult to speculate on reasons for this. However, we have noted in our reply to the comments of reviewer 1 that similar effects have been seen for O₃ uptake to carbonaceous surfaces.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1809, 2002.

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