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Atmospheric
Chemistry
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Discussions

Interactive comment on “Ozone decomposition kinetics on alumina: effects of ozone partial pressure, relative humidity and state of film oxidation” *by* R. C. Sullivan et al.

R. C. Sullivan et al.

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The authors would like to thank the anonymous reviewers for their helpful comments and suggestions.

Reviewer #1

Response to Comments:

1) The units of pressure were changed in the original manuscript to the units of mbar, as previously suggested.

2) The reviewer is correct that there are likely hydroxide groups present on the surface. Eng. et. al. (2000) reported the structure of a hydrated alumina surface to be an intermediate between alpha-Al2O3 and gamma-Al(OH)3 with the surface terminated

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by a monolayer of OH under ambient conditions. Water adsorbs in a partly ordered monolayer on top of the OH-terminated surface. Goodman et. al. (2003) found that complete monolayer formation occurred on alpha-Al2O3 at 17% RH for 296 K. Our alumina powder was stored in its original container until being coated on the pyrex tube. We can assume that the powder had previously adsorbed an appreciable amount of water and is more accurately described as being a mixture of alpha-Al2O3 and gamma-Al(OH)3. Although our alumina films were exposed to a vacuum of less than a few thousandths of a millibar by a rotary vacuum pump we did not heat our surfaces prior to the kinetic experiments (see below). Thus it is reasonable to assume that our alumina surfaces were hydrated when prepared and that much of this water was not removed by storage in the purge box or by the vacuum prior to the exposure to ozone (Al-Abadleh and Grassian, 2003). Grassian (2002) reports that infrared spectroscopy shows oxide powders still retain some adsorbed water even after pumping overnight. We have modified the paper's text to suggest this possibility and its implications on the kinetics and mechanism of ozone decomposition. The effect of pretreating the surface with acid or base is an interesting idea but one that we did not explore. Pretreating the alumina surface with a gas such as NH3 or HCl may impede the ozone decomposition kinetics if the pretreating gas adsorbs to the alumina surface and blocks reactive sites, similar to the proposed effect of water vapour. Hanning-Lee et. al. (1996) reported preliminary results that saturating alpha-Al2O3 with HCl(g) reduced the rate of ozone decomposition, particularly at the lower end of the temperature range studied (213 to 473 K).

3) Ångstroms was changed to nm in the original paper, as previously suggested.

4) The clean air used for the purge box came from a commercial gas purifier designed for purging FTIR spectrometers (Kaesar Model KLDW10). Typically such systems emit lower than ppm levels of hydrocarbons but there are no formal specifications for this specific unit. We note, however, that the cartridges in the unit, used for purging water and carbon dioxide, are filled with alumina. Therefore any volatile organics present in

the input air supply will probably be scavenged within the air supply unit. That being said, it is possible that organic impurities in the methanol may have coated the alumina surface. If so, the more volatile organic contaminants will have been removed by the vacuum pumping prior to the experiments (recall that the vacuum pump had a liquid nitrogen trap installed in-line to prevent the back-streaming of pump oil which could coat the alumina surfaces with organics). If any less volatile contaminants were present, these may have not have been removed and could remain on the alumina's surface and interfere with the rate of ozone decomposition. As the alumina surface used was not characterised chemically, it is impossible to say if such contamination did occur, but we acknowledge the possibility and its potential importance.

5) As discussed above, we agree that our alumina surfaces were probably not entirely dry. Other researchers have observed a change in the ozone decomposition kinetics when the surface is heated prior to the experiment. For example, Hanisch and Crowley (2002) heated some of their Saharan dust samples to 450 K for 5 hours under vacuum before exposing the sample to ozone in a Knudsen cell. They found that the uptake coefficients were higher by a factor of about two for the heated versus unheated samples at an [O3] = 8 E12 molec cmˆ-3. While their Saharan dust system differs from our alumina surface, it is reasonable to assume that similar behaviour would be observed for the alumina surfaces. While we recognise the importance of the effect of drying out the alumina surface on the uptake kinetics, we decided not to investigate this effect as we wished to use alumina surfaces that were typical of realistic dust in the troposphere. Heating the alumina film prior to exposure to ozone would produce an alumina surface much drier than what we would expect to exist under typical tropospheric conditions.

6) Rewording of the Conclusion will be performed in the final version of the text.

7) Although this has been included in other papers on this subject, it is a nevertheless a good suggestion to make estimates of the lifetime for ozone loss under different mineral dust surface area conditions. Such back-of-the-envelope calculations will be included in the ACP version of the paper.

8) Figure 4b was modified and has the data from the first oxidation going off scale at about 55 s. Any flattening out of the data that was previously observed was most likely a result of the [O3] going below the limit of quantification and being strongly affected by the noise in the detection system.

9) In the revised version of the paper there will be a comment made in the caption for Figure 6 with respect to the typical uncertainty associated with each point. We note here (and will note in the text in the error discussion section on page 1987) that there is considerably more scatter in Figure 6 than can be attributed to these individual sources of error. This suggests that the reactivity of the individual films vary somewhat from film to film, for reasons that are not immediately evident.

Reviewer #2

Response to Specific Comments:

1) In our discussion of the role of relative humidity on ozone loss kinetics (section 3.5) we proposed that the reactive ozone chemistry is much more exothermic than the physisorption of the water to the alumina surface. We did not intend to suggest that the heat liberated by the adsorption and decomposition of the ozone would warm the alumina surface and thus prevent the adsorption of water. We merely wished to point out that the decomposition of ozone is likely much more energetically favourable than the adsorption of water. We also pointed out that adding the water vapour and ozone simultaneously may not have allowed enough time for the water vapour to adsorb sufficiently to the alumina surface to have an effect on the rate of ozone loss. As motivated by comments from Reviewer #1, we will also note in the revised version of the paper that considerable amounts of strongly-bound water may have resided on the film, even under our "dry" conditions.

2) As we did not characterise chemically our alumina film surfaces we cannot be sure that all the methanol solvent was removed by drying in the purge box and subsequent exposure to vacuum. If traces of methanol did remain one effect would be to block

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reactive sites on the alumina film's surface, as water vapour is proposed to do. It is possible that this gives rise to some of the scatter in the data in Figure 6 which can not all be attributed to uncertainties in the initial ozone concentration used and in the film's surface area. However, we note that Hanisch and Crowley (2001) used ethanol and water to disperse their films of alpha-Al2O3, CaCO3 and authentic dust samples in their study of the reactivity of HNO3 with these surfaces. Both solvents gave the same results for all four surfaces. We used methanol as it evaporates much more quickly than water does. We also prepared films by spraying a suspension of the alumina onto the glass tube using a nebuliser (DeVillbiss) but found that dripping a slurry of the alumina and then rolling the tube produced much more uniform and controllable films.

3) Yes, each data point in Figures 5 & 6 represents the first time that that alumina film had been exposed to ozone. We have modified the figure caption text in the revised version to make this explicitly clear.

4) BET surface measurements were made on alumina films prepared in the same way as those films used for the kinetic studies. However, the uncertainties in measuring the adsorption of a very small amount of krypton gas required that we perform the BET measurements on alumina films of at least 100 mg. This mass of alumina is at the upper limit of what can be reasonably measured for the ozone kinetics experiments; higher film masses have ozone decay rates that are too fast to quantify. Thus the same alumina films used for the BET measurements were not used for the ozone kinetics experiments. Both sets of alumina films were prepared in exactly the same manner, only the mass (and thus surface area) of alumina differed. In this regard, the wording in the original version of the text will be clarified.

5) The reference for the ozone absorption cross section at 254 nm (1.150 E-17 cmˆ2) is: Sander, S.P. et al., Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 14, JPL Publication 02-25, 2003.

6) The reviewer has a good suggestion for the title of the ACP paper: It will be changed

to "Ozone decomposition kinetics on alumina: Effects of ozone partial pressure, relative humidity and repeated oxidation cycles"

Response to Technical Corrections:

1) We have rewritten the sentence following (R1) in section 3.6 to make it clearer.

2) Figure 4: ACP publishes in colour so hopefully this will make the symbols more distinguishable. Also, the control experiments are the only data using open symbols, again to increase the clarity.

3) Figure 6: We have attempted to improve the clarity of the axis labels and changed the symbol used for N2.

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