

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.

Anonymous Referee #1

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The authors address a significant problem– quantifying the interaction of atmospheric mineral dust with ozone, starting with a well defined system Al_2O_3 . They have a unique experimental approach that is commendable for having measured the BET area of the surface in situ and because it investigated the role of water vapor. This would not have been possible in the low pressure environment of a Knudsen cell. Their approach to the subject has been thorough and professional. I have only a few comments:

Why not use SI units of mbar or hPa for pressure? If you insist on using Torr, please note that it should be capitalized.

The discussion for the reaction mechanism involves some speculation. I am not convinced that there are $\text{Al}(0)$ active sites in Al_2O_3 (or possible oxidation states other than

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Al(III). Can the authors present any evidence or references to support this assertion? It is likely that there will be Al-OH groups on the surface, why they have not been discussed? A related question, would the surface reactivity change if the sample was pretreated with gas phase acid (e.g. HCl) or base (e.g. NH₃)?

Angstroms should be spelled Ångstroms.

How can the authors be sure that there are not unsaturated hydrocarbons present on their surfaces, and that this is due to part of the surface reactivity? Hydrocarbons could be introduced as impurities or contamination in the methanol, or in the purge air. What measures were taken to ensure the purity of the purge air?

It was very interesting to see the author's results concerning the non-effect of relative humidity on the reactivity of the surface. However, I am not convinced that they started the experiment with a dry surface– the results may have been different if elevated temperatures had been used to drive the water off the surface. A room temperature purge for 54 hours is not sufficient to remove all surface adsorbed water. Nonetheless, the results are useful from an atmospheric perspective.

In general the English is excellent. I recommend a slight rewriting of the first line of the Conclusions section, e.g. 'Our findings are in complete agreement with previous investigations showing that there is....'

In the section 'Conclusions and atmospheric implications,' I feel that the authors have not attempted to address the key question motivating this work– if atmospheric dust has a reactivity (γ) similar to that they have found for alumina, could this explain the ozone depletions described for example by Prospero et al. 1995? A straightforward model of the mass transfer coefficient and ozone lifetime in average and extreme dust loading conditions would be a welcome addition to this section. See for example Li, Perreau, Covington...Grassian, Heterogeneous reactions of volatile organic compounds on oxide particles.... JGRA 106, 5517 - 5529, 2001.

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Figure 4b, is the first oxidation data showing saturation at 60 - 70 s (it appears to flatten out), please discuss in the text.

Figure 6, can you make an estimate of the error bars for your data points? Please add to figure caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1977, 2004.

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