Atmos. Chem. Phys. Discuss., 6, S5825–S5827, 2006
www.atmos-chem-phys-discuss.net/6/S5825/2006/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica" *by* J. Savarino et al.

J. Savarino et al.

Received and published: 29 December 2006

We thank Christof Janssen for his interesting remark about the molecular beam reaction. In his comment three issues are raised.

1/ The translational energy of the parent molecules in the experiment of van den Ende et al. (1982). We agree with him about the inadequacy of these experiments to simulate atmospheric chemical conditions. The kinetic energy involved in the molecular beam reaction is well above the thermal condition encounter in the troposphere/stratosphere. We initially miss this important observation and thank him for alerting us. We have therefore modified the sentence presenting this experiment and now the kinetic energy issue is clearly stated. The fact that the translational energy is so high is unfortunately a characteristic of molecular beam studies, as one wants to have the less dispersive possible beam. However, we want to stress that the general and quite simplistic idea

of breaking one bond is easier than braking two bonds is also a notion that underestimates the dynamics. This was our main motivation to cite van den Ende's work; to alert that other mechanisms are possible. When NO molecule approaches the central atom of ozone and attempts to abstract it, it can lead to a configuration where all O atoms and bonds in ozone are equivalent. The ring isomer of ozone (symmetry D3h) is a well-known structure in theoretical works of the ozone molecule (Muller et al., 1998).

Furthermore, the kinetic of this reaction presents some anomalous behaviour such a curvature of the Arrhenius plot (log(k) vs 1/T plot) already at temperature relevant to atmospheric chemistry (Borders and Birks,1982). The fact that the activation energy is temperature dependent can be partially understood by the presence of two product channels with differing energetic barriers. The initial idea of two PES leading to two different O abstraction atoms in ozone has now been abandoned due to the strong coupling between 2B and 1A2 PES of NO2. However, as stated by Adler-Golden (1989), the idea of two dynamically distinct NO+O3 channels as suggested by the beam experiments is fully compatible with a single ground electronic surface, leaving open the question of the existence of the central O atom abstraction channel. We hope that the laboratory experiments we are conducting will answer this important question.

2/ Inappropriate Viswanathan reference The reference was originally cited because we felt that the introduction section of this paper was a good review of the experimental observations of the NO+O3 reaction, but like CJ we feel now that this reference is inappropriate and is replaced by a second van den Ende's molecular beam study.

3/ The disagreement between Viswanathan and van den Ende works Well, we have another opinion on this issue. In their theoretical work, Viswanathan and Raff considered just the end O atom abstraction configuration, as demonstrated by their Figure 1. Obviously, they cannot reach the same conclusion than van den Ende et al. but this does mean that they are at odds with each other. Actually, the scattering angle found by Viswanathan and Raff (157°) is between the two angles found by van den Ende (180° and 120°).

ACPD

6, S5825–S5827, 2006

Borders, R. A. and Birks, J. W., High-precision measurements of activation energies over small temperature intervals: Curvature in the Arrhenius plot for the reaction NO + O3 –> NO2 + O2, J. Chem. Phys., 86, 3295-3302, 1982.

Adler-Golden, S. M., The NO + O and NO + O3 reactions. Analysis of NO2 continuum chemiluminescence, J. Phys. Chem., 93, 691-697, 1989.

Müller, T., Xantheas, S. S., Dachsel, H., Harrison, R. J., Nieplocha, J., Shepard, R., Kedziora, G. S. and Lischka, H., A systematic ab initio investigation of the open and ring structures of ozone, Chem. Phys. Lett., 293 (1-2), 72-80, 1998.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8817, 2006.