Atmos. Chem. Phys. Discuss., 8, S5506–S5510, 2008 www.atmos-chem-phys-discuss.net/8/S5506/2008/ © Author(s) 2008. This work is distributed under the Creative Commons Attribute 3.0 License.



ACPD 8, S5506–S5510, 2008

> Interactive Comment

Interactive comment on "The role of ice in N₂O₅ heterogeneous hydrolysis at high latitudes" *by* R. L. Apodaca et al.

Anonymous Referee #1

Received and published: 1 August 2008

General Comments:

This paper describes new field measurements of nocturnal nitrogen oxides, principally N2O5, in a polluted arctic environment. The aim is to characterize the conversion rate of NOx, emitted from urban sources in Fairbanks, AK, to soluble nitrate (nitric acid or aerosol nitrate). The authors argue that dark reactions involving N2O5 are the most important mechanism for this conversion, so the results of this study are important to the lifetime of NOx in the arctic.

The paper argues that particle growth and the availability of ice surfaces limit the lifetime of N2O5 and therefore NOx at high values of RH. This conclusion is based on the behavior of the N2O5 lifetime only near 100% RH. The paper also demonstrates



little influence of submicron aerosol from pollution sources in Fairbanks. These are important new results.

The paper does require several corrections, as outlined in the specific comments below. While it is important that these comments are considered and some modifications made to the development of the arguments in the paper, none of the comments below should change the main conclusions of the paper.

Specific Comments:

Page 12597: Reaction (R4) not balanced - no oxygen is produced in this reaction.

Page 12599: regional NOx sources near Fairbanks - is there any biogenic contribution that is significant on the scale of anthrpogenic NOx from Fairbanks?

Page 12600: strong temperature inversions - how important is stratification in analysis of the data here? If there is significant up/down transport, it may affect interpretation of steady states.

Also, issues of particle volatilization in sampling with the DRUM system, referred to later in the manuscript, should be described in the experimental section.

Page 12601: The assumptions for the kinetic loss equation is not that the system is in steady state but rather that there is an equilibrium between reactions R2 and R3. Steady state is the result of setting the differential in equation (1) to zero. The interesting aspect of this analysis is that if the term, k4[N2O5] competes with thermal dissociation of N2O5 (i.e., k3[N2O5]), then the equilibrium between NO3 and N2O5 will no longer hold. Some comparison of these two rate coefficients might be useful, either here or later in the paper.

Page 12603: Conditions for rejection of data for SS analysis. The threshold value for NO seems somewhat arbitrary, unless it is related to an instrumental limit. Data for NO > 1 ppbv should actually achieve rapid steady state if N2O5 is measurable at all for these cases, since there would be a very rapid NO3 sink that should pull the system

8, S5506–S5510, 2008

ACPD

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



closer to steady state. Do measurements agree with a steady state predicted by the presence of NO?

Page 12604: How is it known that wind speeds are uniformly below 3 m s 1 throughout the lowest 1200 m? Wind profiler data available?

Page 12605: Following source rate as opposed to integrating it. Since it is likely that variations in all measured concentrations are the result of transport of pollution plumes of varying intensity, it would seem that the N2O5 concentrations would likely follow the source strength regardless of whether they were in steady state or integrating the source. The argument regarding integration of the source could be developed by estimating the total amount of N2O5 observed against the total amount formed. Such an analysis seems to be possible given the arguments presented to this point that the transport time from the source in Fairbanks is known. Thus, if the production rate coefficients and transport time from source are known, the integral referred to here could be explicitly calculated.

Also, not clear where the 1 ppbv hr-1 Ox loss rate comes from. The production rates given for reaction R1 at 100 pptv hr-1 would not give this Ox loss rate. The Ox loss from the more rapid reaction of NO with O3 could give this Ox loss rate, though this is not the aging that is referred to here.

Page 12606: RH values above 100% - how far above 100% is reasonable? Is there potential for error in the RH measurement for values to 105 or 108%, which seem very large? The arguments regarding saturation with respect to ice would still be valid, even if many of these data were much closer to 100%.

Page 12608: For large diameter particles inferred here, it would be more appropriate to use the uptake rate coefficient expression of Fuchs & Stugnin (Fuchs, N. A., and A. G. Stugnin (1970), Highly Dispersed Aerosols, Ann Arbor Science, Ann Arbor, MI.) rather than equation 3.

ACPD

8, S5506–S5510, 2008

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$k = c^{*}gam^{*}N^{*}pi^{*}r^{2}[1+gam^{*}(0.75+0.283^{*}Kn(r))/(Kn(r)[Kn(r)+1])$

Kn(r) = 3*D/(r*c)

Where N is the particle number density (monodisperse) and D is the N2O5 gas phase diffusion coefficient. The correction term (in brackets) should make a difference for particles of this size.

Page 12609: Discussion of Figure 7. The measured particle number densities show concentrations of 103 cm 3, which is much larger than the values of 1 cm3 quoted earlier in the paper. The authors should use consistent numbers or explain if different assumptions / measurements apply to different air masses. The presence of larger particle number densities bolsters the argument for large surface areas near ice saturation, though it changes the calculation of the actual surface area.

If 20% of the aerosol mass in Fairbanks is sulfate, what is the rest? How much nitrate is in the aerosol? The presence of nitrate in the aerosol is known to suppress N2O5 hydrolysis (Hallquist, M., D. J. Stewart, S. K. Stephenson, and R. A. Cox (2003), Phys. Chem. Chem. Phys., 5, 3453-3463; Mentel, T. F., M. Sohn, and A. Wahner (1999), Physical Chemistry Chemical Physics, 1, 5451-5457), but would not do so at very high RH, where particle growth would reduce the nitrate concentration (activity). This mechanism would also be consistent with the observations of short lifetimes at high RH.

Page 12611: Some further detail on deposition loss to the snow surface would be helpful here - is it possible, for example, to estimate a deposition velocity? Is the depth of the mixed layer known?

Page 12612: To my understanding, the Dentener and Crutzen model study did not fit a value of 0.1 for gamma to observations, but rather applied this value to their model based on laboratory data available at the time. It is not really clear that their model "requires" such a large gamma value. ACPD

8, S5506–S5510, 2008

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12595, 2008.

ACPD

8, S5506–S5510, 2008

Interactive Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

