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Comment

## ***Interactive comment on “An experimental technique for the direct measurement of N<sub>2</sub>O<sub>5</sub> reactivity on ambient particles” by T. H. Bertram et al.***

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Received and published: 22 May 2009

We thank Referee 1 for their comments; below we provide responses to each comment individually. In the following, **R** indicates the referee comment and **A** the authors response.

**R1:** One potential problem with this method, which is common to most probe methods, is that the act of adding N<sub>2</sub>O<sub>5</sub> could change the particles acidity because of HNO<sub>3</sub> formation. I suggest the authors consider this effect. Perhaps a mass-balance analysis could tell you whether or not this could be a large enough effect that it will change  $\gamma$ ?

**A1:** We have added a section (4.5) that addresses the effects of added N<sub>2</sub>O<sub>5</sub> on parti-

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Discussion Paper





cle chemical composition and in turn how that can alter the measured  $k_{het}$ . Increases in  $k_{het}$  resulting from an increase in acidity are relatively minor, however an increase in  $\text{NO}_3^-$  has the potential to significantly alter the retrieved  $k_{het}$  at high  $[\text{N}_2\text{O}_5]_{initial}$  and low particle surface area ( $S_a$ ). As outlined in section 4.5, we argue that at  $[\text{N}_2\text{O}_5]_{initial} < 1$  ppbv, and at ambient  $S_a$  our retrieved  $k_{het}$  is at most 20% lower than the true  $k_{het}$ .

Added to text

#### 4.5 Changes to ambient particle composition

Reactions occurring within the flow reactor can also potentially change the chemical composition of sampled ambient particles, biasing the measured  $k_{het}$ . The uptake of  $\text{N}_2\text{O}_5$  results in the production of at most two particle phase nitrate ( $\text{NO}_3^-$ ) ions for each  $\text{N}_2\text{O}_5$  reacted. Laboratory observations have shown that elevated particle phase  $\text{NO}_3^-$  can limit  $\text{N}_2\text{O}_5$  reactivity [e.g., Wahner et al., 1998]. Thus, at low ambient  $S_a$  loadings and high  $[\text{N}_2\text{O}_5]$  initial conditions, particle phase  $\text{NO}_3^-$  accumulation, stemming from  $\text{N}_2\text{O}_5$  uptake in the flow reactor, can lead to a negative bias in the measured  $k_{het}$ .

We assess these effects using the time-dependent box model described in section 2. Assuming  $[\text{N}_2\text{O}_5]_{added} = 1$  ppbv (typical for our experiments),  $\gamma_{true} = 0.03$ ,  $S_a$  (ambient) =  $200 \mu\text{m}^2\text{cm}^{-3}$  and the flow conditions describe in section 3, we calculate that  $0.35 \mu\text{g m}^{-3}$  of particulate  $\text{NO}_3^-$  is produced in the flow tube. Using characteristic ambient mass loadings and composition and assuming the upper limit that all of the  $\text{NO}_3^-$  remains in the particle phase, we estimated our retrieved  $k_{het}$  to be at most 20% lower than the true  $k_{het}$ , based on the measured effects of  $\text{NO}_3^-$  on  $\gamma(\text{N}_2\text{O}_5)$ , as reported by Wahner et al., [1998]. These results are supported by the strong linearity in  $k_{het}$  observed between 0 and  $1000 \mu\text{m}^2\text{cm}^{-3}$  as shown in Fig. 8. However, we note that experiments run at significantly higher  $[\text{N}_2\text{O}_5]_{initial}$  and similar  $S_a$  will likely be subject to stronger  $k_{het}$  effects.

**R2:** The authors seem to be coy about revealing the other aspects of this work such as whether or not substantial  $\text{ClNO}_2$  (or  $\text{Cl}_2$ ) formation was observed.

**A2:** The reactor, as deployed for the Boulder observations was not configured to look for reaction products (such as  $\text{ClNO}_2$ ). We feel it is a logical conclusion of the results presented herein that: if reactant loss can be detected, and products can be measured by the same CIMS method with similar sensitivity, then this technique could be extended to look for  $\text{ClNO}_2$  production as has been done in the laboratory. Thus, we feel it is appropriate to acknowledge this possible application in the conclusions section. (p 709, line 13).

**R3:** What is the reason for the large difference in uptake between 5% RH and 50% RH in the lab study with malonic acid? It doesn't seem like the 50% RH particles would contain liquid water, so what is causing this effect?

**A3:** Malonic acid is a highly hygroscopic dicarboxylic acid. Laboratory results have shown significant  $\text{H}_2\text{O}$  (liq) at 50% RH (i.e.,  $[\text{H}_2\text{O}]_{\text{liq}} > 15\text{M}$  at 50% RH, 298K), indicating malonic acid particles generated from an atomizer and brought directly to 50% RH are aqueous. In contrast, at <5% RH malonic acid particles are likely crystalline. [Braban and Abbatt, 2004]. The distinction between aqueous and crystalline particles was made on page 705, line 8 and the Braban and Abbatt paper was referenced there. In addition, these results are in agreement with previous laboratory studies of  $\text{N}_2\text{O}_5$  reaction on malonic acid particles by Thornton, et al PCCP 2003, also referenced in the manuscript.

**R4:** Bertram et al., 2009 should be referenced as unpublished work.

**A4:** This has been done

**R5:** Section 6.ii Not sure about this, since your residence time is 8 minutes you might not see the effect of a 'pulse'. The reactor is somewhere between well mixed and plug flow. You could determine its characteristics by just turning the  $\text{N}_2\text{O}_5$  source on and off slowly ie. A step function. Have you tried that?

**A5:** As shown in Figure 10, short duration "pulses" in NO can clearly upset the de-

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termination of  $\gamma(\text{N}_2\text{O}_5)$ . However as the reviewer noted, and Figure 10 indicates, the “pulse” is somewhat smoothed by mixing in the reactor. During sampling cycles where the ambient NO was rapidly fluctuating, the observed and expected decay are vastly different. This approach allows us to formulate an algorithm by which “contaminated” decays can be filtered and excluded from the analysis. We have indeed tried turning the  $\text{N}_2\text{O}_5$  source on and off and looking for the arrival time in  $\text{N}_2\text{O}_5$  at the base of the reactor. This gives similar results to those shown in Figure 3, which were used to empirically assess the flow characteristics (discussed on page 697)

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