

***Interactive comment on* “Temperature thresholds for polar stratospheric ozone loss” by K. Drdla and R. Müller**

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Review of “Temperature thresholds for polar stratospheric ozone loss” by K. Drdla and R. Müller

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The main message of this paper by Drdla and Muller is that polar stratospheric clouds (PSCs) are not a prerequisite for efficient chlorine activation, and hence not for subsequent ozone loss. The authors argue that the binary (H₂SO₄-H₂O) aerosol, when sufficiently cold around the NAT equilibrium temperature (TNAT), suffices to have effective chlorine activation, say within a few days. Conversely, any additional acceleration of chlorine activation caused by PSC formation, i.e. by significant HNO₃ uptake by liq-

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uid or solid aerosols would play a secondary, if not negligible role. This is an important, but obviously also controversial statement.

This paper is not based on new data, but assembles different aspects about PSCs previously described in the literature, and from there arrives at the above statement. I share the authors' view that the paper approaches an important problem and requires the combination of several different points. From my perspective these points are:

(1) The use of the latest JPL recommendation on chlorine activation rates on/in liquid (binary, ternary) stratospheric aerosols, including their ability to process chlorine also at temperatures at or slightly above TNAT. (2) The discussion of the JPL recommended and other chlorine activation rates on NAT surfaces. (3) The reduction of available reactive NAT surface in the case of very low NAT nucleation rates and, hence, very low NAT number densities. (4) The further reduction of reactive NAT surface in case of the NAT particles not achieving thermodynamic equilibrium with the gas phase.

The paper mentions all these four points, but I feel that some improvements in terms of clarity and precision will be required. I try to provide some suggestions and question for revision below.

General concerns:

A clarified description is required in describing the chlorine activation on NAT: namely the approach of using directly data from Hanson and Ravishankara (1993) or alternatively using the parameterization provided by Carslaw and Peter (1997) based on the measurements of Abbatt and Molina (1992) and then extrapolated to stratospheric conditions. As Susan Solomon already pointed out, only the former approach is backed up by the JPL recommendations. I do understand that the authors state that even when H&R93 is applied the expected NAT surface area reduction makes activation on NAT still smaller than that on liquids, but this is hidden on P. 28695 L. 10-12 and should be discussed with care. Furthermore, the question should be addressed whether the surprises of the Arctic winter 2009-2010 with unexpectedly large NAT occurrence (Pitts et

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al., 2010) could potentially compromise the statement that NAT surface area reductions make activation on NAT smaller than that on liquids.

Detailed points:

Abstract, L. 9: "At typical stratospheric conditions, TACL is similar in value to TNAT". This is vague, please provide a number. Also, have a comma after TNAT.

Abstract, L. 10: "...the highest temperature at which nitric acid trihydrate (NAT) can theoretically condense to form PSCs". Replace "can theoretically condense to" by "can exist and". The adverb "theoretically" appears later again, and it remains unclear whether this is meant to express that often a high nucleation barrier hinders NAT formation "practically".

Introduction, P. 28689, L. 19: Sentence hard to understand: "Multiple particle compositions exist simultaneously in the stratosphere." Probably this should read: "Particles of different physical state and composition may coexist in the same stratospheric air parcel."

Introduction, P. 28690, L. 3: "The transition from binary H₂SO₄/H₂O particles to STS particles, in principle, is continuous". Why "in principle"?

Het. Chem. on NAT, P. 28692, L. 21: "SA" is not, as the authors say, the total surface area of the particle type, but the surface area density, and units are for example micrometer²/cc. I would rather call this "SAD".

Het. Chem. on NAT, P. 28692, Eq. (1): I am confused by Eq. (1). The dimensions of k are 1/s, but what does k mean? I would find the following two quantities useful (for the HCl+ClONO₂ reaction): $\# \text{reactions}/(\text{volume} \times \text{time}) = 1/4 \gamma \times n_{\text{ClONO}_2} \times v_{\text{ClONO}_2} \times \text{SAD}$, where γ is a function of HCl concentration, or the corresponding second order rate coefficient: $k(\text{II}) = 1/4 \gamma \times v_{\text{ClONO}_2} \times \text{SAD} / n_{\text{HCl}}$

Het. Chem. on NAT, P. 28692, L. 22: v is the "mean molecular" velocity of the gas-phase reactant.

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Het. Chem. on NAT, P. 28693, L. 5: Why divided by the product of both reactants? I would understand if $\# \text{reactions}/(\text{volume} \times \text{time})$ was divided by $n\text{ClONO}_2$, but a division by $n\text{HCl}$ seems not justified as γ is not linearly dependent on $n\text{HCl}$. The subsequent sentence stating that this normalization would reduce the sensitivity is a bit mystic.

Het. Chem. on NAT, P. 28693, L. 8: Why complete activation? Not sure what is meant. Should this not be reduction of reactants (e.g. of ClONO_2) to $1/e$ of its original value? (Strictly, "complete activation" will only be achieved after an infinite time?)

Het. Chem. on NAT, P. 28693, L. 11: These three "distinct assumptions" could be formulated much more distinctly: (1) NAT nucleates promptly once temperature drops below TNAT . (2) NAT nucleates in a large fraction of the preexisting aerosol particles, i.e. $n\text{NAT} \sim 10/\text{cm}^3$ (not sure where the $1/\text{cm}^3$ derives from that the authors use). (3) Chlorine activation on NAT occurs according to Hanson and Ravishankara (1993) (i.e., not according to the parameterization provided by Carslaw and Peter (1997) extrapolated from the measurements of Abbatt and Molina (1992)).

Het. Chem. on NAT, P. 28693, L. 22: Much better would be: "Based on Carslaw et al. (1997b) we suggest considering two schemes for Reactions R1–R3 on NAT particles, one based on the measurements by Hanson and Ravishankara (1993) as an upper limit, and one based on the measurements by Abbatt and Molina (1992) as the lower limit." I do not think that Carslaw and Peter made such a suggestion by themselves, we just compared and faced the dilemma that the A&M data made physically more sense, but required far extrapolations to arrive at stratospheric conditions, whereas the H&R experiments were directly probing the relevant conditions but did not fit together with the extrapolated A&M data.

Het. Chem. on NAT, P. 28693, L. 26: What is "the lower limit scheme"? It would be better, if the authors clearly stated that they introduce two scenarios: "Upper limit scheme": fixed values for γ s based on chlorine activation rates on NAT according to Han-

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son and Ravishankara (1993). "Lower limit scheme": parameterization provided by Carslaw and Peter (1997), extrapolated from the measurements of Abbatt and Molina (1992). At least this is what I think is meant.

Het. Chem. on NAT, P. 28693, L. 26: "... based on Abbatt and Molina (1992)". Probably you mean: based on Carslaw and Peter's interpretation of the Abbatt and Molina measurements?

Het. Chem. on NAT, P. 28693, L. 28: How is this possible? Seems too large a reduction! Three orders of magnitude? According to Carslaw and Peter (1997), AM92 values should be 2 orders of magnitude lower than HR93 values, not 3 orders of magnitude (compare solid and long-dashed lines in Fig.2a of Carslaw and Peter for the HCl+ClONO₂ reaction, and similar their Fig.2c for the HCl+HOCl reaction.

Het. Chem. on NAT, P. 28694, L. 8: "... uncertain, but the freezing mechanism that converts liquid particles to NAT probably plays a critical role." This statement is trivial, skip?

Het. Chem. on NAT, P. 28694, L. 18: The attribution of the term "NAT rocks" is incorrect: Fahey et al. did not call these particles "NAT rocks", rather Fueglistaler et al. (ACP, 2002).

Het. Chem. on NAT, P. 28695, L. 2: Yes, the NAT clouds typically develop only very low particle number densities and grow slowly. But this requires a citation. Already Biele et al. (2001) noted that NAT particles in such low number densities "...do not have enough time to develop their equilibrium size, that is, they absorb only a small fraction of the available HNO₃ ... This is a surprising finding at first sight, as. at most. 5% of the total available HNO₃ is allowed to condense".

Het. Chem. on NAT, P. 28695, L. 9: Note that a similar figure as Fig.1 has been shown by Dameris et al. (Chem. Unserer Zeit, 2007, 41, 152 – 168, DOI: 10.1002/ciuz.200700418). They also explicitly mention that NAT clouds with low num-

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ber densities do not reach equilibrium with the gas phase and reach surface area densities typically lower by at least 2 orders of magnitude compared with conditions corresponding to maximum NAT nucleation (see their Fig. 9).

Het. Chem. on Liquids, P. 28696, L. 6: “Therefore” should be replaced by “In this approximation, ...”. Also, there was some work by the Molina group which might be useful to justify this approximation...

Het. Chem. on Liquids, P. 28695, L. 18: “. . .the aerosol contains a negligible fraction of gas-phase HNO₃”. Replace “gas-phase HNO₃” by “the total available HNO₃”.

Discussion, P. 28701, L. 26: “As long as most particles remain liquid, the chemistry in these models is comparable to the liquid aerosol chemistry adopted here.” This is strictly true only if non-equilibrium effects are taken into account (or if HNO₃ uptake is artificially limited).

Discussion, P. 28702, L. 25: See also Schraner et al., ACP 2008.

Figure 1, caption, L. 1: How is “chlorine reactivity” defined?

Figure 1, caption, L. 3: “NAT reactivity relative to the most simple assumption on NAT PSCs (“NAT, Original”)”. What is the “most simple assumption”? Unclear.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28687, 2010.

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