

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

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General comments

We thank T. Peter for his review and the helpful comments provided.

One important, general concern he raised was the use of the JPL recommendation (Sander et al., 2006). The current JPL recommendation (Sander et al., 2006, Table 5-2) for reactions on NAT surfaces is a constant γ -value, e.g., for R1 $\gamma = 0.2$. The work of Carslaw and Peter (1997)) is mentioned briefly in note 76 of Table 5-2 of Sander et al. (2006), but this cannot be interpreted as a recommendation. In Fig. 1 of the paper we use both the constant recommended γ -values and a temperature dependent γ -value

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employing the lower limit scheme for NAT reactivity (Carslaw et al., 1997; Carslaw and Peter, 1997) based on the measurements by Abbatt and Molina (1992). All assumptions are now clearly stated in the paper. A similar figure to Fig. 1 has been published by Dameris et al. (2007), who used the upper limit scheme based on the measurements by Hanson and Ravishankara (1993) for the NAT reactivity and obtained the same basic result, namely that the time scale for heterogeneous chlorine activation of a typical NAT cloud is much longer than that on liquid aerosol particles; this study is now mentioned and cited in the paper. Regarding liquid particles, we use the parameterization by Shi et al. (2001) for the reaction R1 on cold liquid sulfuric acid aerosol, which is the study put forward in the current JPL evaluation (Sander et al., 2006), although no clear cut recommendation is given. Using the work of Hanson (1998) instead, leads to very similar activation time scales on liquid aerosol for temperatures between 192–195 K. The text has been revised throughout the paper to bring these points across more clearly.

A second important issue raised in the review is the question of the reduction of the reactive NAT surface area by first, low NAT number densities and, second, NAT particles not reaching equilibrium with the gas-phase. As suggested, both issues are discussed now in the paper much more extensively and more literature is cited (as suggested in the detailed comments). We are confident that these changes make the presentation of the issue of reactive NAT surface area more traceable to the reader.

Further, as suggested, we discuss in more detail the CALIPSO PSC observations. We state now that Pitts et al. (2010) find that 13% of the CALIPSO PSC observation between 2006–2010 fall into the a categorie (Mix 2-enh) of NAT particles with relatively high number density ($> 0.1\text{cm}^{-3}$) embedded in an STS cloud. In the extremely cold Arctic winter period in January 2010, there were significantly more observations of this type of PSC (and of ice PSCs) than before (Pitts et al., 2010). However, it is important to note that these observations were made a temperatures well below T_{NAT} and that the “NAT, Original” calculation assumed an even greater NAT concentration of 1cm^{-3} .

Further, the Mix 2-enh clouds are mixtures so that the chlorine reactivity is not a pure NAT reactivity but rather a mixture of STS and NAT reactivity. Finally, higher number density liquid/NAT mixtures, were primarily observed by CALIPSO downstream of wave ice clouds, where substantial chlorine activation has probably occurred. This effect should reduce the importance of the Mix 2-enh clouds for chlorine activation in general and in particular for the onset of activation.

In summary, we feel that we have addressed all the issues raised in the review and that the paper has been improved through these changes. All minor comments (see below) were taken into account.

Response in detail

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

The difference is 1-2 K and we have mentioned this in the abstract now.

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".

We agree, done.

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".

Thanks, done.

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

"in principle" has been dropped.

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".

We agree, we now say "surface area density" here and throughout the paper.

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): #reactions/(volume x time) = 1/4 gamma x nClONO₂ x vClONO₂ x SAD, where gamma is a function of HCl concentration, or the corresponding second order rate coefficient: k(II) = 1/4 gamma x vClONO₂ x SAD / nHCl

Equation (1) is the pseudo-first-order loss rate of a heterogeneous reaction (Hofmann and Solomon, 1989; Brasseur and Solomon, 2005). The intention in formulating the chlorine reactivity in this way it is done in the paper, is to obtain a measure of the mean activation (averaged over all activation pathways R1–R3). The focus on individual reactions, as suggested in the review, is a different way of addressing the problem, the study by Wegner et al. (2011) will adopt this complementary point of view. We have now (in the text and the caption) very clearly described how the chlorine reactivity has been calculated.

Het. Chem. on NAT, P. 28692, L. 22: v is the "mean

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molecular" velocity of the gas-phase reactant.

Thanks, done.

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.

We agree that the sentence on normalization is confusing and it was dropped. γ may be dependent on HCl , but not for all parameterizations. Especially, note that the JPL recommendation still is constant γ . As stated above, the intention here is to obtain a measure of the mean activation.

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?)

The language here was imprecise. The point is the initial titration of ClONO_2 against HCl (a value for $1/e$ would not be substantially different). The sentence reads now: "above TNAT there is no chlorine activation but 1 K below TNAT the initial activation step [...] takes only one day".

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. $n\text{NAT} 10/\text{cm}^3$ (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

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according to the parameterization provided by Carslaw and Peter (1997) extrapolated from the measurements of Abbatt and Molina (1992)).

We agree with the first two points and have changed the text accordingly. (the value of 1/cm³ for NAT particles was used in the literature in the past in several models (e.g., Krämer et al., 2003)). Regarding (3), for the extreme increase in reactivity in case "NAT, Original", more is required than using a parameterization based on Hanson and Ravishankara (1993). This scenario is only possible for NAT formation at saturation ratio one and for constant gamma values (see Fig. 5 in Krämer et al., 2003).

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.

The text was changed as suggested, which we think is consistent with what Carslaw et al. (1997) say (who actually use the terms upper and lower limit).

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 gammas based on chlorine activation rates on NAT according to Hanson and Ravishankara (1993). "Lower

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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.

We agree. We have changed the text to make this point clear.

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?

Yes we do – text changed.

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.

Correct, the AM92 values are 2 orders of magnitude lower than HR93 values as stated slightly above in the paragraph. However, the "NAT, Original", case is *not* based on Hanson and Ravishankara (1993). This scenario assumes NAT formation at saturation ratio one and constant gamma values (comparable to some models in Fig. 5 in Krämer et al., 2003).

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?

We agree, done.

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).

It is correct to say that Fahey et al. did not use the term "NAT rocks" in their paper, however, people (e.g. RM) certainly remember that Dave Fahey called the large NAT particles he and his group detected during the SOLVE campaign in 2000 "NAT rocks" when he talked about his findings during the campaign in Kiruna. We have added the citation to the Fueglistaler et al. paper and believe that this covers all aspects.

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".

Thanks for the comment. We have added the following text: "Furthermore, growth of NAT particles is slow compared to the length of cold periods, especially in the Arctic (e.g., Peter, 1997; Dameris et al., 2007). Slow growth of NAT particles was indeed observed by Biele et al. (2001) in Lidar measurements in the Arctic".

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 number 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

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nucleation (see their Fig. 9).

Thanks for the comment. We agree and have now added: "A similar figure to Fig. 1 was published by Dameris et al. (2007), who used the upper limit scheme based on the measurements by Hanson and Ravishankara (1993) for the NAT reactivity and obtained the same basic result, namely that the time scale for heterogeneous chlorine activation of a typical NAT cloud is much longer than that on liquid aerosol particles".

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.

Text replaced as suggested. And we have added a sentence on the work by the Molina group: "This assumption is supported by laboratory studies by Elrod et al. (1995), who find that γ -values for liquid H₂SO₄-HNO₃-HCl-H₂O solutions for Reaction (R1) remain essentially unchanged when HNO₃ uptake on the liquid particles is neglected".

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".

Text replaced as suggested.

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).

We agree. The point is not that the activation rates are strictly equivalent; we have therefore used a somewhat weaker formulation: "the chlorine activation rates in these models are rather similar in magnitude to those deduced from the liquid aerosol chemistry adopted here"

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

Citation has been added.

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.

The caption has been extended to provide the necessary information. The relevant section now reads: "Chlorine reactivity is calculated by summing the loss rates of both ClONO₂ and HCl due to reactions (R1)–(R3). The resulting total is divided by the sum of the concentration of ClONO₂ and HCl. For the "NAT, Original" case, NAT is assumed to form immediately at TNAT. The surface area is calculated assuming all excess HNO₃ condenses (i.e., NAT is at equilibrium) and a NAT concentration of 1 cm⁻³. The reaction probabilities on NAT are assumed to be constant, specifically 0.2 for (R1), 0.004 for (R2), and 0.1 for (R3) (Sander et al., 2006, Table 5-2)."

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