Reply to "Comment on 'Do NAD and NAT Form in Liquid Stratospheric Aerosols by Pseudoheterogeneous Nucleation?'"

Daniel A. Knopf[†]

Institute for Atmospheric and Climate Sciences, IAC, ETH Zürich, Zürich, Switzerland

Received: September 29, 2006

In her comment, Tabazadeh[1] raises several points of criticism on the work by Knopf:[2] (1) the paper does not provide new experimental and theoretical studies to debate the main conclusion of Tabazadeh et al.,[3] i.e., the possibility of a pseudoheterogeneous nucleation process occurring in polar stratospheric clouds (PSCs) to form NAD (nitric acid dihydrate) and NAT (nitric acid trihydrate), (2) Knopf[2] ignores experimental and theoretical studies supporting pseudoheterogeneous nucleation, (3) nucleation rates are not expected to equal zero at the melting points of NAD and NAT using the framework of classical nucleation theory (CNT), (4) adjustment of the activation energies in the parametrization[3] yields suitable pseudoheterogeneous nucleation rates (PNR), (5) Knopf[2] lacks the treatment of atmospheric disequilibrium processes as encountered, e.g., in mountain lee waves. Here Knopf responds to these points.

(1) As mentioned in Knopf,[2] a possible pseudoheterogeneous nucleation mechanism is not ruled out, but it is shown, that the upper limits of the PNRs of NAD are too small to explain observations of large nitric acid containing particles (LNACP) in number densities of about 10^{-4} cm^{-3} in synoptic PSCs.[4] These findings are in agreement with two more recent studies.[5,6] Knopf[2] follows a similar analysis of Tabazadeh et al.[3] but uses a more extensive NAD and NAT nucleation data set compared to Tabazadeh et al.'s[3] that also includes nucleation in supercooled $HNO_3/H_2SO_4/H_2O$ solution droplets. Tabazadeh et al.[3] neglected data sets of Koop et al.[7,8] and Bertram et al.[9] without further discussion, and those have been shown[2] to disagree with the PNR parametrization.[3] For these reasons, Knopf's new analysis provides more conservative upper limits of the PNRs under relevant stratospheric conditions.[2]

(2) Knopf[2] investigates pseudoheterogeneous nucleation occurring in aqueous HNO_3 and aqueous HNO_3/H_2SO_4 solution droplets. The general idea of pseudoheterogeneous nucleation may be supported by recent experimental and theoretical studies applying pure water droplets,[10−15] as mentioned by Tabazadeh.[1] However, one should proceed with caution when transferring nucleation characteristics obtained from pure water droplets to droplets containing aqueous electrolytic solutions. It is well-known that nucleation characteristics such as nucleation temperature and phase change significantly when electrolytes are added to pure water.[16,17]

(3) Tabazadeh et al.[3] fit the activation energies linearly as a function of S. This is in disagreement with classical nucleation theory (CNT)[18] and results in finite PNR values, J, at the melting point of the crystal. Correct employment of the CNT framework would result in a logarithmic dependency between the activation energy and S, which leads to the correct thermodynamic behavior of $\lim_{S\to 1} J = 0$, i.e., the PNR approaches 0 as the melting point of the crystal is reached.[18] As shown in Knopf,[2] employing all available nucleation data sets, which cover $S < 10$, the PNRs behave according to CNT.

(4) A change in the activation energy by 1 kcal mol^{-1} changes the PNR by a factor of 14. A 10% adjustment of the activation energy could lead to changes of 3 kcal mol^{-1} in the activation energy under stratospheric conditions. Such an arbitrary adjustment of the pseudoheterogeneous activation energy may result in the correct representation of the observed particle numbers but does not provide evidence that the particles indeed formed by pseudoheterogeneous nucleation. Additionally, decreasing the activation energy by 10% may result in disagreement with laboratory data used to derive the concept of pseudoheterogeneous nucleation.[3]

(5) The nucleation rates derived by Knopf et al.[19] and Knopf[2] are discussed for equilibrium conditions typically encountered in synoptic scale PSCs, as has been done by Tabazadeh et al.,[3,20] and others.[7−9,21−23] Knopf et al.[19] and Knopf[2] found that neither homogeneous nucleation nor pseudoheterogeneous nucleation, respectively, are sufficient to explain LNACP (10^{-4} particles cm^{-3}). Tabazadeh[1] addresses other atmospheric scenarios in which particles and gas phase may be in disequilibrium. Such disequilibrium events may be encountered in mountain lee waves with particle number densities much higher than 0.1 cm^{-3}. To address these points, the reader is referred to the work of Meilinger et al.,[24] Tsias et al.,[25] and Luo et al.,[26] the last discussing various nucleation scenarios for S values up to 500.

Although Tabazadeh et al.[3] mention caveats within their analysis, many modeling studies are using this parametrization to deduce if pseudoheterogeneous nucleation occurred under atmospherically conditions. These include two very recent studies of Tabazadeh,[27,28] although the author is aware of the problematic extrapolation of PNRs to stratospheric conditions.[1] Knopf points out that a PNR parametrization that is thermodynamically not sound and that is in disagreement with laboratory data cannot be used to determine nonambiguously if pseudoheterogeneous nucleation of NAD occurred in synoptic PSCs.[2] An adjusted PNR parametrization[1,27] may be used as a first approximation to describe the atmospheric particle observations, but from this it cannot be concluded that LNACP were formed by a pseudoheterogeneous nucleation mechanism.

References and Notes

(1) Tabazadeh, A. *J. Phys. Chem. A* **2006**, *111*, 1374.
(2) Knopf, D. A. *J. Phys. Chem. A* **2006**, *110*, 5745−5750.
(3) Tabazadeh, A.; Djikaev, Y. S.; Hamill, P.; Reiss, H. *J. Phys. Chem. A* **2002**, *106*, 10238−10246.
(4) Fahey, D. W.; et al. *Science* **2001**, *291*, 1026−1030.
(5) Stetzer, O.; Möhler, O.; Wagner, R.; Benz, S.; Saathoff, H.; Bunz, H.; Indris, O. *Atmos. Chem. Phys.* **2006**, *6*, 3023−3033.
(6) Möhler, O.; Bunz, H.; Stetzer, O. *Atmos. Chem. Phys.* **2006**, *6*, 3035−3047.
(7) Koop, T.; Biermann, U. M.; Luo, B.; Crutzen, P. J.; Peter, T. *Geophys. Res. Lett.* **1995**, *22*, 917−920.
(8) Koop, T.; Luo, B. P.; Biermann, U. M.; Crutzen, P. J.; Peter, T. *J. Phys. Chem. A* **1997**, *101*, 1117−1133.
(9) Bertram, A. K.; Dickens, D. B.; Sloan, J. J. *J. Geophys. Res.* **2000**, *105*, 9283−9290.
(10) Shaw, R. A.; Durant, A. J.; Mi, Y. *J. Phys. Chem. B* **2005**, *109*, 9865−9868.
(11) Sastry, S. *Nature* **2005**, *438*, 746−747.
(12) Lu, Y. J.; Xie, W. J.; Wei, B. *Appl. Phys. Lett.* **2005**, *87*, 184107.
(13) Durant, A. J.; Shaw, R. A. *Geophys. Res. Lett.* **2005**, *32*, L20814.
(14) Backus, E. H. G.; Grecea, M. L.; Kleyn, A. W.; Bonn, M. *Phys. Rev. Lett.* **2004**, *92*, 2707−2709.
(15) Vrbka, L.; Jungwirth, P. *J. Phys. Chem. B Lett.* **2006**, *110*, 18126−18129.

[†] E-mail: knopf@chem.ubc.ca. Now at Department of Chemistry, University of British Columbia, British Columbia, Canada.

10.1021/jp066423q CCC: $37.00

(16) Koop, T. *Z. Phys. Chem.-Int. J.* **2004**, *218*, 1231−1258.

(17) Murray, B. J.; Knopf, D. A.; K. B. A. *Nature* **2005**, *434*, 202−205.

(18) Pruppacher, H. R.; Klett, J. D. *Microphysics of Clouds and Precipitation*; Kluwer Academic Publishers: Netherlands, 1997.

(19) Knopf, D. A.; Koop, T.; Luo, B. P.; Weers, U. G.; Peter, T. *Atmos. Chem. Phys.* **2002**, *2*, 207−214.

(20) Tabazadeh, A.; Jensen, E. J.; Toon, O. B.; Drdla, K.; Schoeberl, M. R. *Science* **2001**, *291*, 2591−2594.

(21) Bertram, A. K.; Sloan, J. J. *J. Geophys. Res.* **1998**, *103*, 3553−3561.

(22) Bertram, A. K.; Sloan, J. J. *J. Geophys. Res.* **1998**, *103*, 13261−13265.

(23) Salcedo, D.; Molina, T.; Molina, M. J. *J. Phys. Chem. A* **2001**, *105*, 1433−1439.

(24) Meilinger, S. K.; Koop, T.; Luo, B. P.; Huthwelker, T.; Carslaw, K. S.; Krieger, U. K.; Crutzen, P. J.; Peter, T. *Geophys. Res. Lett.* **1995**, *22*, 3031−3034.

(25) Tsias, A.; Prenni, A. J.; Carslaw, K. S.; Onash, T. P.; Luo, B. P.; Tolbert, M. A.; Peter, T. *Geophys. Res. Lett.* **1997**, *24*, 2303−2306.

(26) Luo, B. P.; Voigt, C.; Fueglistaler, S.; Peter, T. *J. Geophys. Res.* **2003**, *108*, 2707−2709.

(27) Irie, H.; Pagan, K. L.; Tabazadeh, A.; Legg, M. J.; Sugita, T. *Geophys. Res. Lett.* **2004**, *31*, 2001−2013.

(28) Pagan, K. L.; Tabazadeh, A.; Drdla, K.; Hervig, M. E.; Eckermann, S. D.; Browell, E. V.; Legg, M. J.; Foschi, P. G. *J. Geophys. Res.-Atmos.* **2004**, *109*, D04312.