

The submission by Bzdek et al. represents a potentially significant contribution for the atmospheric research community in that it suggests the importance of the role of amines in new particle formation. While atmospheric ammonia concentrations are typically 2-3 orders of magnitude greater than that of amines, the results presented by Bzdek et al. indicate that small salt clusters (< 3 nm) are most likely aminium salts rather than ammonium salts. This is based on the experimentally determined free energy of exchange of amines for ammonia in salts, which was highly exothermic (i.e. $\Delta G < 0$) and secondly, that the reverse substitution reactions (i.e. ammonia displacing the amine) were not observed. Also, the uptake coefficient was near unity, which as the authors note, implies that the complete exchange of ammonia by amines may happen in the atmosphere on a time scale of seconds to minutes.

Specific comments and questions that should be addressed prior to publication:

- 1) Regarding Eq. 9 for the Langevin rate constant, k_L : In that expression k_L looks to be in the form of the Langevin-Gioumousis-Stevenson expression. In that case, the constant should be 2π , not 2.342, as the authors have written. The authors are calculating the capture collision rate constant by the method of Su and Chesnavich.¹ The expression for k_L in that work and in their earlier publication on this method,² is similar to the expression used by Bzdek et al., with the exception of the constant multiplicative factor, which was 2π in Chesnavich et al.² and is 2.342 in the current submission. The value of the constant impacts directly calculation of the collision rate, which in turn affects calculation of the reactive uptake. Although this discrepancy, which is a factor of 2.683, will not impact the authors' conclusions, this point should be either clarified by Bzdek et al., or corrected.
- 2) In regards to Eq. (11) and Eq. (12): The dimensionless parameter τ has a continuous slope at the boundary $\tau = 2(2)^{1/2}$, i.e. $k_{SC}/k_L = 1.57$ in Eq. (11) and Eq. (12) at this value of τ . Hence τ should be expressed: $0 < \tau \leq 2(2)^{1/2}$ in Eq. (11), and $\tau \geq 2(2)^{1/2}$ in Eq. (12). Also, it is not clear from the manuscript that $k_{\text{collision}}$ in Eq. (14) is calculated from k_{SC} , which I learned was the case only by reading the original papers by Su and Chesnavich. Some discussion should be provided in the manuscript regarding the difference between the two rate constants and the explicit mathematical relation between $k_{\text{collision}}$ and k_{SC} .
- 3) Regarding Table 1: The authors are reporting the uptake coefficient (γ) as $\gamma = k_{II}/k_{\text{collision}}$. Working some of these numbers out, it appears that the values of γ for the first and third entries under the substitution with NH_3 are inverted ($<3.8 \pm 1.1 \times 10^{-4} \leftrightarrow <1.9 \pm 0.6 \times 10^{-4}$). Also, the authors state that the error on k_{II} is constant at 30%. Is this an experimentally measured error or is it propagated from errors in k_I and P_{gas} ? If the latter, a simple treatment of propagation of error yields (for the quotient $k_{II} = k_I/P_{\text{gas}}$) a final relative error on k_{II} of 20% (assuming the error reported for k_I in Table 1 and a relative error of 21% in the pressure measurement, as stated in the manuscript). If this is correct, the second and third entries of the second order rate constants column (for substitution reactions with DMA) should read: $9.3 \pm 2.0 \times 10^{-10}$ and $9.7 \pm 2.0 \times 10^{-10}$, as opposed to both having error of ± 3.0 as the authors have listed. Also in Table 1, there are minor errors in the calculated values of γ for the 1st and 3rd entries. The correct values are 0.846 (or 0.85) and 0.746 (or 0.75), respectively (assuming the authors' calculation of k_L is correct, cf. comment 1).

- 4) It would be useful if the authors listed in a Table or stated in text the volume polarizability (α') and the dipole moment (μ'_D) of ammonia and the amines. This would allow for τ to be calculated readily, which is needed for calculation of the capture collision rate. The authors may want to consider adding values of the volume polarizability and the dipole moment to Table 4.
- 5) In the Supplemental information, k_2 for exchange of a second DMA for ammonia is given as 0.41 ± 0.03 . This is slightly different from the value in Table 1, which is 0.41 ± 0.02 . There is also a slight discrepancy in the error for k_3 .

References

1. Su, T.; Chesnavich, W. J., Parametrization of the ion-polar molecule collision rate constant by trajectory calculations. *J. Chem. Phys.* **1982**, *76* (10), 5183-5185.
2. Chesnavich, W. J.; Su, T.; Bowers, M. T., Collisions in a noncentral field: A variational and trajectory investigation of ion-dipole capture. *J. Chem. Phys.* **1980**, *72* (4), 2641-2655.