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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Comparative study on the heterogeneous reaction between methylamine and ammonium salts" *by* Y. Liu et al.

Anonymous Referee #1

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This work investigates the interaction between methylamine (MA) and four ammonium salts, ammonium nitrate (AN), chloride (AC), sulfate (AS), and bisulfate (ABS), using a Knudsen cell reactor coupled with a quadrupole mass spectrometer (QMS) and in situ Raman spectrometer. Displacement reactions were observed between MA and AN, AC and AS, while MA reacted with ABS via an acid-base reaction mechanism, which was confirmed by changes in several signature peaks in Raman spectra. The uptake coefficients of MA on all four ammonium salts were determined from the Knudsen cell-QMS experiments and were comparable to other recent studies. For the uptake of MA on AN, AC and AS, their DFT calculation suggested a linear relationship between uptake coefficients and the electrostatic potentials of ammonium ions in these salts. The results from this manuscript further support the possibility for atmospheric amines to incorporate into particle phase by reacting with ammonium salts widely observed in

ambient aerosols. Major Comments: 1) One concern regarding this study is its novelty relevant to the current literature, since similar kinetic measurements have been reported previously and it is no obvious what new insight on the reaction mechanism has been provided in the present work. The authors need to clearly address such an issue. 2) Another problem with this paper is the analysis of their experimental data. For example, their discussion about the relationship between uptake coefficients and ammonium salt mass used in the Knudsen cell-QMS experiments (Page 177, line 6-29) was weakened since there was no estimation on the ratio between amine and ammonium salts reacted during the reaction. Their work indicated that whether the mass of ammonium salts affects amine uptake coefficients is still under debate. However, no attempt was made to assess the discrepancies among previously reported values by analyzing the reaction stoichiometry, i.e., what reactant was more abundant in the reactor within the reaction timescale. 3) The issues for decomposition of AN and AC were not well addressed. Was the result in Fig. 3(F) carefully checked, since AC has a dissociation constant similar to that of AN (Ge et. al. 2011a)? Note that the dissociation of AN and AC can also affect the reaction stoichiometry. 4) The dissociation of methylammonium nitrate (MAN) and methylammonium chloride (MAC) under vacuum condition does not necessarily suggest that the reaction between MA and AN/AC is "partially" reversible (Page 176, line 3-4 and line 10-11). This may only indicate that MAN/MAC is not stable at high vacuum condition and has a higher dissociation vapor pressure than methylammonium sulfate. Additional experiments where aminium salts are exposed to gaseous ammonia are required to clarify if the reaction is reversible. Other comments: 1) The title appears a bit confusing since it is unclear whether the study focuses on the differences in the reactivity of ammonium salts or attempts to compare the current experimental data with previous measurements. 2) Due to decomposition of AN under high vacuum, it may be more appropriate to discuss Raman data first to confirm reaction mechanism. 3) Fig. 6, there is no point to include ABS since the ammonium ion in ABS is not involved in the uptake reaction based on Eq. R(3). 4) Page 166, the last sentence, the correct reference to the experimental study of

amines in nanoparticle growth is Wang et al. (Nature Geosci. 3, doi:10.1038/ngeo778, 238-242, 2010).

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