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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.

Y. Liu et al.

ycliu@rcees.ac.cn

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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.

Response: We thank Referee #1 for the comments and suggestions on our manuscript.

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.

Response: Thank you. As you mentioned, the reaction mechanism for MA on these ammonium salts are the same as that reported in the literatures. Several papers also reported the uptake coefficients of some amines on (NH4)2SO4. However, our paper is mainly focused on the difference in reactivity of MA on different ammonium salts. This is the first time to investigate this issue. It is also the first time to report the uptake coefficients of MA on NH4NO3, NH4HSO4, and NH4Cl. In our manuscript (page 168, Lines 10-11), we have pointed out that at present date, it is not clear yet that how the property of inorganic ammonium salts affects the reactivity for this reaction. This might be not so strong. As you suggested, we further addressed this issue more clearly in our revised manuscript as follows:

"At present date, the reported uptake coefficients showed a discrepancy among different ammonium salts. However, it is hard to directly compare these results because of the difference in reaction conditions, such as the particle size, the type of amines and ammonium salts, and the reaction temperature used in experiments and so on. On the other hand, the relatively few kinetic data is available for one kind of amine. For example, as for MA, only Qiu et al. (2011) reported its uptake coefficient on (NH4)2SO4. The uptake coefficients of MA on other salts are unknown. Thus, it is not clear yet that how the property of inorganic ammonium salts affects the reactivity for this reaction. In this study, we investigated the heterogeneous uptake of MA on NH4HSO4, (NH4)2SO4, NH4NO3 and NH4Cl to understand the effect of ammonium salts on their reactivity with MA. We established for the first time the structure-reactivity relationship between MA and ammonium salts.”

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.

Response: Thanks. According to your suggestion, we calculated the ratio between amine and ammonium salts reacted during the reaction. When the QMS signal intensity (I) was calibrated with molecular flow rate (molâĂćs-1) (Liu et al., 2008), the amount of MA uptake onto ammonium salts can be calculated using the integrated area shown in Fig. 1. They are 6.0×10-7, 1.1×10-6, 1.2×10-6, and 3.9×10-7 moles on (NH4)2SO4, NH4HSO4, NH4NO3, and NH4Cl, respectively. The amount of ammonium salts are 4.4×10-4, 5.3×10-4, 7.5×10-4 and 1.2×10-3 moles, respectively. Therefore, the ratios between uptaked amine and ammonium salts during the reaction are estimated to be 0.14 %, 0.21 %, 0.16 % and 0.03 % on (NH4)2SO4, NH4HSO4, NH4NO3, and NH4Cl, respectively. If two ammonium ions in (NH4)2SO4 involve in the exchange reaction, the ratio should be 0.07 %. It means than only a very small fraction of ammonium salts, most probably confined on the surface, involves in this heterogeneous reaction. This paragraph was also added in our revised manuscript.

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.

Response: Thanks. We carefully checked the data for decomposition of AC. It is very difficult to discern the dissociation of NH4Cl from the raw data, while when the raw data of HCl was magnified 3 times, desorption of HCl can be observed with the Ah of 5.5 mm2. Therefore, pure AC should also dissociate under our experiment conditions. In our revised manuscript, we corrected it as follows: “Fig. 3F shows the desorption of NH3 and HCl (m/e=36, 3 times of magnification) from pure NH4Cl. It was almost unobservable for desorption of NH3 and HCl with the Ah of 0.88 mm2; while a weak desorption of NH3 and HCl can be discerned when the Ah was increased to 5.5 mm2. It meant that dissociation of both NH4Cl and CH3NH3Cl should contribute to the signals in Fig. 3D. According to the value of I17/∆I30=0.27 and the change of signal intensity of m/e=30 in Fig. 3D, we estimated that decomposition of CH3NH3Cl contributes 12 % to the intensity change of the m/e=30 in Fig. 3D. Thus, we can conclude that CH3NH3NO3 and CH3NH3Cl are not stable at low pressure and they have higher dissociation vapor pressure than methylammonium sulfate.” The revised figure was also replaced.

Fig. 3

As you pointed out that dissociation of AN and AC might also affect the reaction stoichiometry. However, we think it is impossible to investigate this effect using our instruments at present.

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.

Response: Thanks. We deleted the sentence “These results also indicate that the exchange reaction between CH3NH2 and NH4NO3 was partially reversible under these conditions.” And in our revised manuscript, we changed the conclusion as “Thus, we can conclude that CH3NH3NO3 and CH3NH3Cl are not stable at low pressure and they have higher dissociation vapor pressure than methylammonium sulfate.” This was also revised in abstract and conclusion.

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. Response: Thanks. As you suggested, we revised the title as “Differences in the reactivity of ammonium salts with methylamine”. It might be clearer than the original one.

2) Due to decomposition of AN under high vacuum, it may be more appropriate to discuss Raman data first to confirm reaction mechanism.

Response: Thanks. In fact, we also discussed Raman data of AN first in Page 173, Lines 9-12.

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).

Response: Thanks. The data of ABS in Fig. 6 was deleted in the revised manuscritpt. Additionally, the y-axis should be shown in logarithmic plot as the requirement for free energy relationship. This was also corrected in our revised manuscript.

Fig. 6

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).

Response: Thanks. The correct reference was added in the revised manuscript.

Reference: Liu, Y. C.; He, H.; Mu, Y. J., Heterogeneous reactivity of carbonyl sulfide on a-Al2O3 and r-Al2O3. Atmos. Environ., 42, 960-969, 2008. Wang, L.; Khalizov, A.F.; Zheng, J.; Xu, W.; Ma, Y.; Lal, V.; Zhang, R.Y.; Atmospheric nanoparticles formed from heterogeneous reactions of organics. Nat. Geosci., 3, 238-242, 2010a.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C1205/2012/acpd-12-C1205-2012-supplement.zip

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 165, 2012.

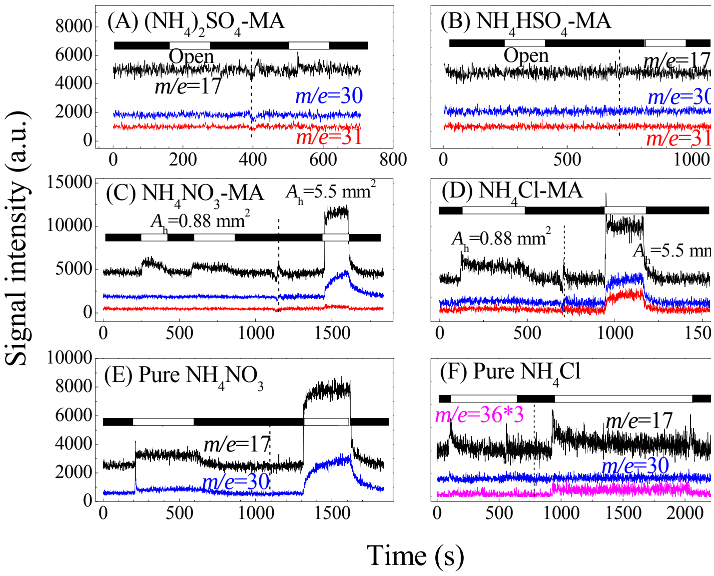
(A) (NH4)2SO4-MA
Open
m/e=17
m/e=30
m/e=31
(B) NH4HSO4-MA
Open
m/e=17
m/e=30
m/e=31
(C) NH4NO3-MA
Ah=0.88 mm2
Ah=5.5 mm2
(D) NH4Cl-MA
Ah=0.88 mm2
Ah=5.5 mm
(E) Pure NH4NO3
m/e=17
m/e=30
(F) Pure NH4Cl
m/e=36*3
m/e=17
m/e=30
Signal intensity (a.u.)
Time (s)
0
2000
4000
6000
8000
5000
10000
15000
200
400
600
800
500
1000
1500
2000

Fig. 3

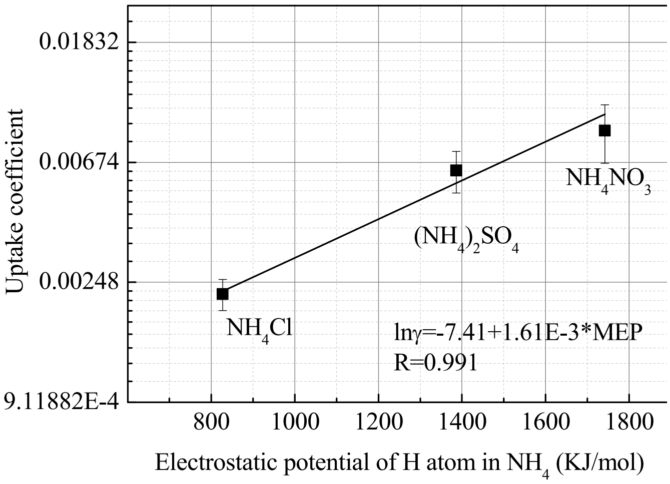
Uptake coefficient
0.01832
0.00674
0.00248
9.11882E-4
800
1000
1200
1400
1600
1800
NH4Cl
(NH4)2SO4
NH4NO3
lnγ=-7.41+1.61E-3*MEP
R=0.991
Electrostatic potential of H atom in NH4 (KJ/mol)

Fig. 6