Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Heterogeneous uptake of amines onto kaolinite in the temperature range of 232-300 K

Y. Liu[1,2,3], Y. Ge[1,3], H. He[1,2,3*]

1. State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
2. Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.
3. University of Chinese Academy of Sciences, Beijing, 100049, China

[*] Correspondence to: H. He (honghe@rcees.ac.cn)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Abstract:

Amines contribute to atmospheric reactive nitrogen (N_r) deposition, new particle formation and the growth of nano- and sub-micron particles. Heterogeneous uptake of amines by ammonium compounds and organic aerosols has been recognized as an important source of particulate organic nitrogen. However, the role of mineral dust in the chemical cycle of amines is unknown because the corresponding reaction kinetics are unavailable. In this study, the heterogeneous uptake of methylamine (MA), dimethylamine (DMA) and trimethylamine (TMA) by kaolinite was investigated in the temperature range of 232-300 K using a Knudsen cell reactor. Lewis acid sites on kaolinite were identified as dominant contributors to the uptake of amines, utilizing Fourier transform infrared spectroscopy. The uptake coefficients (γ) were derived from the mass accommodation coefficients based on the temperature dependence of the γ. The initial effective uptake coefficients (γ_{eff}) were $(2.27\pm0.26)\times10^{-3}$, $(1.71\pm0.26)\times10^{-3}$ and $(2.95\pm0.63)\times10^{-3}$, respectively, for MA, DMA and TMA on kaolinite at 300 K, while they increased ~3-fold with decreasing temperature from 300 K to 232 K. The adsorption enthalpies (ΔH_{obs}) of MA, DMA and TMA on kaolinite were -7.8 $\pm$0.8, -9.9 $\pm$2.9 and -9.4 $\pm$1.0 kJ mol^{-1}, respectively, and the corresponding entropy values (ΔS_{obs}) were -77.1$\pm$3.2, -84.1$\pm$11.8 and -80.6$\pm$3.7 J K^{-1} mol^{-1}. The lifetimes of MA, DMA and TMA attributable to heterogeneous uptake by mineral dust were estimated to be 7.2, 11.5 and 7.7 h, respectively. These values were comparable to the lifetimes of amines consumed by OH oxidation. Our results reveal that uptake by mineral dust should be considered in models simulating the chemical cycle of amines in the atmosphere. The results will also aid in understanding the possible impacts of amines on human health, air quality, and climate effects.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

1.0 Introduction

Over the past 200 years, atmospheric emissions of nitrogen-containing compounds have increased significantly due to increased anthropological emissions from intensive fossil-fuel combustion, agricultural activity and animal husbandry (Keene et al., 2002). This has amplified atmospheric reactive nitrogen (N_r) concentrations and increased atmospheric N_r deposition rates (Meunier et al., 2016). These elevated N_r fluxes may significantly perturb terrestrial, aquatic, estuarine and coastal marine ecosystems (Liu et al., 2013;van Breemen, 2002). However, reliable predictive capabilities for the impacts of N_r on ecosystem require the accurate quantification of the deposition fluxes (Keene et al., 2002) as well as the transformation of atmospheric N_r. Amines, whose atmospheric concentrations are typically 1~14 nmol N m^{-3} and 1-2 orders of magnitude lower than that of ammonia (Ge et al., 2011;Qiu and Zhang, 2013), are emitted into the atmosphere from marine organisms, animal husbandry, biomass burning, sewage treatment, meat cooking, automobiles and industrial processes (Zhang et al., 2012). Compared with inorganic nitrogen, the budget and the atmospheric chemistry of organic nitrogen, including amines, are still poorly characterized (Keene et al., 2002;Cornell et al., 2003).

Amines may contribute 10–20% of the organic content of ambient particles, and over one hundred different amine species have been frequently observed in the particle phase (Qiu and Zhang, 2013). It has been recognized that acid-base reactions between amines and nitric acid (Murphy et al., 2007), sulfuric acid (Almeida et al., 2013;Jen et al., 2014;Bzdek et al., 2011;Wang et al., 2010a), and methanesulfonic acid (MSA) (Nishino et al., 2014) contribute to nucleation (Smith et al., 2010;Almeida et al., 2013), and growth of nano- and sub-micron particles (Qiu and Zhang, 2013). Heterogeneous uptake of amines onto $(NH_4)_2SO_4$ (Bzdek et al., 2010a;Qiu et al., 2011;Chan and Chan,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

2012), NH_4HSO_4 (Qiu et al., 2011;Liu et al., 2012a;Chan and Chan, 2012), NH_4NO_3 (Liu et al., 2012a;Chan and Chan, 2012;Lloyd et al., 2009), NH_4Cl (Liu et al., 2012a;Chan and Chan, 2012), humic acid, and citric acid (Liu et al., 2012b) has been proposed as another possible explanation for particulate amines observed in ambient particles. The uptake coefficient (γ) of amines on ultra-fine nanometer-scale ammonium particles is close to unity (Bzdek et al., 2010b), whereas it is on the order of ~10^{-3}-10^{-2} on coarse particles (Qiu et al., 2011;Liu et al., 2012a) and fine particles of 20-500 nm particle diameter (Lloyd et al., 2009). The γ of amines on citric acid and humic acid is on the order of ~10^{-3} and ~10^{-5} (Liu et al., 2012b), respectively. Similar to the reaction between NH_3 and secondary organic aerosol (SOA) (Liu et al., 2015b;Nguyen et al., 2013;Lee et al., 2013b) or between $(NH_4)_2SO_4$ and glyoxal (Galloway et al., 2009;Trainic et al., 2011;Yu et al., 2011;Lee et al., 2013a), carbonyl groups in organic aerosol can also take up primary and secondary amines to form imine and enamine compounds in both bulk solution and the particle phase (Zarzana et al., 2012;De Haan et al., 2009). This may explain the high-MW constituents with a large fraction of carbon–nitrogen bonds observed in ambient particles (Wang et al., 2010b).

Mineral dust, with a global source strength of 1000-3000 Tg year^{-1}, is one of the most important contributors to atmospheric particles and plays an important role as a reactive surface in the global troposphere (Dentener et al., 1996). The reactive uptake of SO_2, HNO_3, NO_2, N_2O_5, O_3 and HO_2 on mineral dust has been widely investigated (Usher et al., 2003) and has been found to significantly influence sulfate (Zheng et al., 2015), nitrate and O_3 formation by affecting trace gas concentrations and the tropospheric oxidation capacity through surface processes (Zhang and Carmichael, 1999). On the other hand, the temperature in the atmosphere varies with latitude, longitude, and altitude above the Earth's surface, as well as with season and time of day.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

For example, the tropospheric temperature for latitude 40 °N during June decreases from room temperature (r.t.) to 220 K with an increase in altitude. The temperature at the tropopause can reach values much lower than 220 K: down to 180 K above the Antarctic in winter (Smith, 2003). For most atmospheric reactions, the reaction kinetics is sensitive to temperature. Thus, it is very important to measure the reaction kinetics (Crowley et al., 2010;Atkinson et al., 2006) and its temperature dependence for trace gases, including amines, (Qiu and Zhang, 2013) on mineral dust in order to fully understand the relevant atmospheric chemistry. However, at the present time, the role of mineral dust in the chemical cycle of amines in the atmosphere is unknown, because the corresponding temperature-dependent reaction kinetics for these reactions is unavailable.

In this work, heterogeneous uptake of amines including methylamine (MA), dimethylamine (DMA) and trimethylamine (TMA) by kaolinite, which has been found to be a typical mineral dust crystalline phase in atmospheric particles, was investigated in the temperature range of 232-300 K. The temperature dependence of uptake coefficients, relevant thermodynamic parameters and associated environmental implications are discussed. The results of this study will aid in understanding the atmospheric chemistry of amines.

2.0 EXPERIMENTAL DETAILS

2.1 Uptake experiments. Uptake of amines was investigated using a Knudsen cell reactor coupled to a mass spectrometer (KCMS). This system has been described in detail elsewhere (Liu et al., 2012b;Liu et al., 2012a;Liu et al., 2010a;Liu and He, 2009 ;Liu et al., 2008 ;Liu et al., 2008). Briefly, the KCMS was composed of three stages with different working pressures. The first one was the Knudsen cell reactor

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

working at ~10^{-4} Torr. It consisted of a stainless steel chamber with a gas inlet controlled by a leak valve, an escape aperture whose area was adjustable using an iris diaphragm, a sample holder attached to the top surface of a circulating fluid bath, and an ion gauge (BOC Edwards). The sample in the sample holder could be exposed to or isolated from the reactants by a lid connected to a linear translator. The temperature of the sample holder was controlled using a thermostat and cryofluid pump (DFY-5/80, Henan Yuhua laboratory instrument Co, Ltd.) and measured with an embedded Pt resistance thermometer. The second stage was a transition chamber pumped by a 60 $L \cdot s^{-1}$ turbomolecular pump (BOC Edwards). The working pressure in this stage was ~10^{-7} Torr and monitored with an ion gauge (BOC Edwards). In the third stage, a quadrupole mass spectrometer (QMS, Hiden HAL 3F PIC) was housed in a vacuum chamber pumped by a 300 $L \cdot s^{-1}$ turbomolecular pump (Pfeiffer) at a working pressure of ~10^{-9} Torr measured using an ion gauge (BOC Edwards).

Kaolinite powder was dispersed evenly on the Teflon sample holder with ethanol, heated at 373 K for 2 h after the solvent was evaporated at room temperature, and then out-gassed at 298 K in the Knudsen cell reactor for 8 h to reach a base pressure of approximately 5.0×10^{-7} Torr. Amine (MA, DMA or TMA) equilibrated with the corresponding aqueous solution was introduced into the reactor chamber through the leak valve. The pressure of amines in the reactor was kept at $3.5 \pm 0.2 \times 10^{-5}$ Torr to ensure free molecular flow in the reactor. The reactor chamber was passivated with amines while the sample was isolated from the reactant gas by the sample cover, until a steady state QMS signal was established. Then, the sample was exposed to the amines for uptake experiments.

The observed uptake coefficients (γ_{obs}) were calculated with a Knudsen cell equation (Tabor et al., 1994; Ullerstam et al. 2003; Underwood et al., 2000), namely,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

$$\gamma_{obs} = \frac{A_h}{A_g} \cdot \frac{I_0 - I}{I} \quad (1)$$

where A_h is the effective area of the escape aperture (0.88 mm^2) during uptake experiments and measured according to methods reported previously (Liu et al., 2009a, b and 2010a, b); A_g is the geometric area of the sample holder (326 mm^2); and I_0 and I are the mass spectral intensities with the sample holder closed and open, respectively. The reaction kinetics were measured in the temperature range of 232-300 K.

Analytical grade MA (40 % in H_2O, Alfa Aesar), DMA (40 % in H_2O, Aladdin Chemistry Co. Ltd) and TMA (28 % in H_2O, TCI), ethanol (Sinopharm Chemical Reagent Co. Ltd) and kaolinite (Aladdin Chemistry Co. Ltd) were used as received. The specific surface area (N_2-BET) of kaolinite was 71 $m^2\ g^{-1}$, measured using a Quantachrome Autosorb-1-C instrument.

2.2 *In situ* infrared spectra measurements. The surface species during uptake of amine by kaolinite were monitored using *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The particles were prepared by depositing small droplets containing kaolinite suspension onto the ATR crystal (ZnSe) with an atomizer, followed by purging with 1 $L{\cdot}min^{-1}$ zero air to obtain dry particles in the ATR chamber. After the particles were dried, which was monitored by observing the IR bands of water, amine vapor was introduced into the reactor by a flow of 200 $mL{\cdot}min^{-1}$ zero air through a water bubbler containing the amine. *In situ* IR spectra were recorded on a Nicolet 6700 (Thermo Nicolet Instrument Corporation, USA) Fourier transform infrared (FTIR) spectrometer equipped with an *in situ* attenuated total reflection chamber and a high sensitivity mercury cadmium telluride (MCT) detector cooled by liquid N_2. The IR spectra were recorded taking the dried kaolinite as reference during uptake of amine. All spectra reported here were recorded at a resolution of 4 cm^{-1} for 100 scans.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

3.0 Results and Discussion

3.1 Uptake of amines on kaolinite at 300 K. Figure 1A, B and C show the typical uptake profiles for MA, DMA and TMA, respectively. Figure 1D, E and F show the corresponding profiles of the observed uptake coefficients, which will be discussed later. In these experiments, the sample mass was ~20 mg and the temperature was held at 300 K. The partial pressures of amines in the reactor were around 5.0×10^{-5} Torr, which corresponded to ~60 ppbv of amines in the atmosphere. Both the molecular ion peak and the largest fragment, i.e. m/z 31 and 30 for MA, m/z 45 and 44 for DMA, and m/z 59 and 58 for the TMA, were scanned to verify that the species were being correctly measured. As shown in Fig. 1A-C, the relative signals of the two monitored mass channels for each amine coincided very well. The normalized QMS signals decreased significantly when the kaolinite samples were exposed to amines. The lowest values of the normalized QMS signal (I/I_0) were 0.45, 0.63, and 0.47 for MA, DMA and TMA on kaolinite, respectively, under this specific condition. Then, the I/I_0 increased gradually with exposure time due to the surface saturation of amines. The uptake behaviors for these amines on kaolinite were similar to those on humic acid as observed in our previous work (Liu et al., 2012b), whereas they were different from the uptake behaviors of amines on ammonium compounds (Liu et al., 2012a). The recoveries of the uptake curves of amines can be explained by the saturation of the surface reactive sites on kaolinite. However, exchange reactions take place between amines and ammonium compounds, resulting in ammonia as the product (Liu et al., 2012a;Qiu et al., 2011;Bzdek et al., 2010a); subsequently, a continuous uptake of amines accompanied by ammonia formation was observed within a certain period of time (Liu et al., 2012a).

Kaolinite is a 1:1 layer mineral. Each layer of the mineral consists of an alumina

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms (Brindley and Robinson, 1945) and repeating layers of the mineral are hydrogen-bonded together (Miranda-Trevino1 and Coles, 2003). Usually, both Lewis acid and Brønsted acid sites are present on metal oxides (Busca, 1999;Benvenutti et al., 1992). Pyridine, piperidine or *n*-butylamine have been widely used as probe molecules to measure the type of acid site and the acidity of metal oxide materials (Busca, 1999). To confirm the reactive sites on kaolinite, infrared spectra were collected using an *in situ* ATR-FTIR.

Figure 2 shows the ATR-FTIR spectra of MA, DMA and TMA adsorbed on kaolinite for 30 min at 300 K. It should be pointed out that the absolute intensities for the bands of surface species resulting from adsorption of different amines were not identical, even for the adsorbed water bands at ~3400 and ~1640 cm^{-1}. This might be related to different mass loading of kaolinite deposited on the ZnSe crystal via atomization. Therefore, we only qualitatively discuss the assignments of the related surface species. The typical IR bands of amines, such as the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ bands at 2962 and 2860 cm^{-1} accompanied by the $\delta(CH_3)$ bands at ~1400 cm^{-1} and the $\rho(CH_3)$ bands from 985 cm^{-1} to 1290 cm^{-1} (Murphy et al., 1993), the overtone/combination bands of $-CH_3$ and CN groups in the range of 2300-2700 cm^{-1} (Murphy et al., 1993), the $\nu_s(CN)$ bands at ~1260 and 850 cm^{-1} (Durgaprasad et al., 1971), $\delta(NH_2)$ of MA at 1606 cm^{-1} (Nunes et al., 2005) and the $\delta(NH)$ band (NIST) and/or $\delta(CH_3)$ of DMA at 1473 cm^{-1} (Lin et al., 2014) in Fig. 2, confirmed the adsorption of amines on kaolinite. In a previous work, the IR bands at 1484 and 984 cm^{-1} were assigned to the characteristic bands of protonated TMA ($(CH_3)_3NH^+$) in an acidic solution mixed with TMA and on the surface of polyethylene (PE) treated by TMA (Ongwandee et al., 2007). In this work, two bands at 1477-1467 cm^{-1} and 971 cm^{-1} were observed, as shown in

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Fig. 2, and were probably related to the protonated amines (MAH^+, $DMAH^+$ and $TMAH^+$). In particular, a strong peak at 1473 cm^{-1} was observed (Fig. 2B), while the band was very weak for the spectra in Fig. 2A and C. However, this band was very close to the δ(NH) band at ~1470 cm^{-1} in DMA (NIST database) and/or $\delta(CH_3)$ (Lin et al., 2014) in amines. On the other hand, it should be noted that formation of protonated amines requires surface OH (Brønsted acid). However, as shown in Fig. 2, the surface hydroxyl (-OH) in the range of 3600-3750 cm^{-1} (Miranda-Trevino1 and Coles, 2003) was not consumed when the kaolinite was exposed to MA, DMA or TMA. This indicates that the content of reactive Brønsted acid sites on the kaolinite must be very low even if the bands at 1477-1467 cm^{-1} originated from the protonated amines. Therefore, Lewis acid sites on the kaolinite predominantly contributed to the uptake of amines as observed in Figs. 1 and 2 in this study. This was similar to the adsorption of DMA and N,N-dimethyl formamide (DMF) on TiO_2, for which Lewis acid sites were identified as the reactive sites (Lin et al., 2014).

As shown in Fig. 1, the saturation times for the amines on kaolinite varied slightly depending upon the number of substituted methyl groups in the amines. For example, the saturation time was ~20 min for MA, while it decreased to ~15 min and ~10 min for DMA and TMA, respectively. This implies a different rate of increase for the surface coverage among the different amines during adsorption. According to the gas-particle equilibrium of amines on the surface of kaolinite as shown in Eq. (2),

$$A_g \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A_s \qquad (2)$$

the surface concentration of amines on kaolinite can be described as,

$$\frac{dc_{A,s}}{dt} = k_a c_{A,g} - k_d c_{A,s} \qquad (3)$$

where k_a and k_d are the adsorption coefficient and desorption coefficient, respectively;

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

$c_{A,g}$ and $c_{A,s}$ are the concentration of amines in the gas phase and on the surface, respectively. When replacing $c_{A,s}$ with the surface coverage of amine ($\theta = c_{A,s}/c_T$), the time dependent surface coverage of amine is

$$\frac{d\theta}{dt} = \frac{k_a c_{A,g}}{c_T} - k_d\theta \quad (4)$$

or,

$$\theta = \frac{k_a c_{A,g}}{k_d c_T} - \frac{1}{k_d}\exp(-k_d t) \quad (5)$$

where c_T is the total reactive or adsorptive sites or the saturated adsorption capacity for amines on kaolinite; t is the exposure time. Therefore, the saturation time of amines on kaolinite depends on the adsorption coefficient, the desorption coefficient, the total number of reactive sites and the concentration of amines in the gas phase. If all the layers of the packed kaolinite particles are assumed to be available to amine molecules, the saturated adsorption capacity of MA, DMA and TMA on kaolinite is estimated to be 1.7×10^{19}, 7.3×10^{18} and 5.7×10^{18} molecules mg^{-1}, respectively, under this reaction condition. These values will be lower if amines cannot penetrate all the layers in the sample holder. This will be discussed later. The adsorption capacities are inversely correlated with the cross-sectional area of MA (0.243 nm^2), DMA (0.323 nm^2), and TMA (0.394 nm^2) (Liu et al., 2012b). This means that a part of the Lewis acid sites accessible to MA on the kaolinite surface would not be accessible to amines with larger molecular volume or cross-sectional area.

3.2 Reaction kinetics of amines on kaolinite at 300 K. Based on the measured QMS signals of amines as shown in Fig. 1, the uptake coefficients were calculated using Eq. (1). Figure 1D, E and F show the evolution of γ_{obs} of MA, DMA and TMA, respectively, as a function of exposure time on kaolinite at 300 K. The initial γ_{obs} varied from ~2.0×10^{-3} to ~3.0×10^{-3} for these amines at 300 K, while the γ_{obs} decreased markedly

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

with increasing exposure time as shown in Fig. 1. This is in agreement with the results observed for most of the reactive gases, such as NO_3, N_2O_5 (Tang et al., 2010), NO_2 (Wang et al., 2012;Ndour et al., 2008;Liu et al., 2015a), O_3 (Hanisch and Crowley, 2003), HONO (El Zein and Bedjanian, 2012) and COS (Liu et al., 2010a) on typical atmospheric particles because of surface saturation, as discussed above.

For packed powder samples in a sample holder, diffusion of reactive molecules into the underlying layers was widely observed in previous works (Liu et al., 2010b;Liu et al., 2010a;Keyser et al., 1991;Underwood et al., 2001;Grassian, 2002). Therefore, the effective uptake coefficient (γ_{eff}) might be overestimated when calculating the γ with Eq. (1) in which the geometric area of the sample holder instead of the effective surface area is considered. The KML model (Keyser et al., 1991), LMD model (Underwood et al., 2001;Grassian, 2002) and FPL model (Hoffman et al., 2003) have been developed to estimate the effective surface area of uptake for heterogeneous reactions. The linear mass dependent (LMD) model (Underwood et al., 2001), which was developed based on the KML model, has been widely used for data interpretation in Knudsen cell experiments. That is,

$$\gamma_{obs}=\gamma_{eff}\, m_{eff}\, S_{BET}/A_g \quad (6)$$

or,

$$\gamma_{eff}= A_g\, Slope/S_{BET} \quad (7)$$

where γ_{eff} is the effective uptake coefficient; m_{eff} is the effective sample mass; S_{BET} is the specific surface area of the sample; A_g is the geometric area of the sample holder; *Slope* is the slope of the plot of γ_{obs} versus sample mass in the linear regime (mg^{-1}). Thus, γ_{eff} can be determined by measuring the m_{eff} of reactive molecules or the slope of the γ_{obs} versus sample mass for multilayer powder samples when the powder samples evenly cover the sample holder.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Figure 3 shows the γ_{obs} of the three amines on kaolinite in the mass range of 20-100 mg at 300 K. When the sample mass was less than 20 mg, the sample holder could not be evenly covered by particles. In such a case, γ_{obs} would be underestimated with Eq. (1). Therefore, uptake experiments with sample mass below 20 mg were not performed. However, as shown in Fig. 3, the γ_{obs} of MA, DMA and TMA were independent of the sample mass of kaolinite within experimental uncertainty. This is similar to the uptake of amines on $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, and NH_4Cl (Qiu et al., 2011;Liu et al., 2012a) and citric acid (Liu et al., 2012b), the uptake of HNO_3 on soot (Muñoz and Rossi, 2002) and N_2O_5 and H_2O on mineral dust (Seisel et al., 2005;Seisel et al., 2004). This indicates that the underlying layers of the kaolinite sample contributed very little to amine uptake.

The probe depth of a reactive gas in a packed powder sample can be expressed by using a factor for the effect of gas-phase diffusion into the underlying layers (Keyser et al., 1991;Underwood et al., 2001).

$$\eta = \frac{1}{\phi}\tanh(\phi) \quad (8)$$

$$\phi = \frac{m}{\rho_b A_g d_p}\left(\frac{3\rho_b}{\rho_t-\rho_b}\right)\left(\frac{3\tau\gamma_{eff}}{4}\right)^{1/2} \quad (9)$$

Thus,

$$\gamma_{obs}=\gamma_{eff}\,(A_e+\eta A_i)/A_g \qquad (10)$$

where η is a factor to account for the effect of gas-phase diffusion into the underlying layers ($0\leq\eta\leq1$); m is the sample mass; ρ_b and ρ_t are the bulk density and the true density of the sample, respectively; d_p is the particle diameter of the sample; τ is the tortuosity factor of the sample; A_g is the geometric area of the sample holder; A_e and A_i are the area of the first layer of the sample (external) and the area of the underlying layers of the sample (internal), respectively. The reactive gas can effectively diffuse into the

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

underlying layers if η is close to 1, while the contribution of the underlying layers to the reactive gas uptake is negligible when η is close to 0. Therefore, a large γ_{eff} should result in a small η or small probe depth, and vice versa. This means that the γ_{eff} of amines on kaolinite should be close to or equal to the γ_{obs} in this study. Thus, the mean γ_{obs} measured at different sample mass were taken as the corresponding γ_{eff} of amines on kaolinite and summarized in Table 1. They were $(2.27\pm0.26)\times10^{-3}$, $(1.71\pm0.26)\times10^{-3}$ and $(2.95\pm0.63)\times10^{-3}$, respectively, for MA, DMA and TMA on kaolinite at 300 K. The γ_{eff} of amines on kaolinite were on the same order as the γ_{eff} of amines on coarse particles, including $(NH_4)_2SO_4$, NH_4NO_3, NH_4Cl and citric acid (Liu et al., 2012a;Liu et al., 2012b) investigated in our previous work, and on 20-500 nm NH_4NO_3 particles (Lloyd et al., 2009), while they were 1 and 3 orders of magnitude lower than that on the surface of a H_2SO_4 solution (Wang et al., 2010a) and ammonium salt clusters (Bzdek et al., 2010b), respectively.

There are several factors affecting the heterogeneous reaction kinetics of amines with the typical components of atmospheric particles. First, particle size plays an important role in the reactivity of amines. For example, the first-order γ of DMA on 1-2 nm $[(NH_4)_3(SO_4)_2]^+$ clusters was close to unity (Bzdek et al., 2010b), while γ decreased to 10^{-3}-10^{-2} on coarse particles of $(NH_4)_2SO_4$ (Liu et al., 2012a;Qiu et al., 2011). Second, strong acidity of a particle or solution favors the reactions between amines and the substrates. The γ of amines on citric acid, with a pK_{a1} of 3.1, were 2 orders of magnitude higher than those on humic acid, with a pK_{a1} of 5 (Liu et al., 2012b). H_2SO_4 solution with higher H_2SO_4 content also showed a slightly larger γ for amines (Wang et al., 2010a). Even for different ammonium compounds, the H with stronger acidity in the NH_4 group showed a higher reactivity toward MA (Liu et al., 2012a). Third, the steric effect of amines has an effect on the reactivity on the same substrate.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

It has been found that the γ of amines on citric acid and humic acid linearly decreased with the cross-sectional area of the amines (Liu et al., 2012b). Finally, reaction conditions such as temperature and humidity should have an influence on the reactivity between amines and particles. Wang et al. (Wang et al., 2010a) observed that the γ of amines negatively depended on temperature due to the negative temperature dependence of the mass accommodation coefficient. This might partially explain the difference in the measured γ of MA on $(NH_4)_2SO_4$ between our previous work (Liu et al., 2012a) and Qiu's work (Qiu et al., 2011). Chan et al. (Chan and Chan, 2012) found that a high RH favored the formation of TEAH sulfate in the displacement reaction between TEA and $(NH_4)_2SO_4$. Under the same reaction conditions, the properties of both the particles and the amines should have an effect on the heterogeneous reactivity of amines.

Figure 4A shows a box chart of the measured γ_{eff} of these three amines on kaolinite at 300 K. Means comparisons were performed with the Dunn-Sidak method. ANOVA analysis demonstrated a statistically significant difference in the mean γ_{eff} among MA, DMA and TMA at the 0.05 level (F=49.3, P=2.54×10^{-13}). The γ_{eff} of MA was significantly larger than that of DMA, while it was significantly smaller than that of TMA. This should be ascribed to the difference in the properties of the amines, because the influence of the particle size and acidity on the reactivity, as mentioned above, can be ruled out when the same substrate is used. The reactivity sequence observed in this study is in contrast with that between amines and organic acids (Liu et al., 2012b). This might be explained by the different types of reactive sites for organic acids and kaolinite toward amines. For organic acids, the –COOH group is the reactive site (Liu et al., 2012b), while Lewis acid sites predominantly contribute to the uptake of amines on kaolinite in this study, as discussed in Section 3.1. The interaction between –COOH and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

amines should be more sensitive to the neighboring groups than that between M^+ (Lewis acid) and amines, because the C-C bonds in organic acid are more flexible than the M-O (metal-oxygen) bonds in kaolinite. This means that the steric effect of amines is unimportant for the reaction between amines and kaolinite. As shown in Fig. 4B, the γ_{eff} of amines on kaolinite are positively correlated with the basicity of amines (H. K. Hall, 1957). Therefore, the slightly higher reactivity of TMA on kaolinite can be explained by its strong basicity and the lower reactivity of DMA on kaolinite should be related to its weak basicity.

3.3 Temperature dependence of amine uptake on kaolinite. Table 2 summarizes the mean γ_{eff} at different temperature. The γ_{eff} were in the range of $(2.27\pm0.26)\times10^{-3}$-$(5.79\pm0.64)\times10^{-3}$ for MA, $(1.71\pm0.26)\times10^{-3}$-$(6.04\pm1.24)\times10^{-3}$ for DMA and $(2.95\pm0.63)\times10^{-3}$-$(9.24\pm0.26)\times10^{-3}$ for TMA. For all three amines, the γ_{eff} increased with decreasing temperature. This is similar to the uptake of amines on the surface of H_2SO_4 solution (Wang et al., 2010a), the uptake of HNO_3, HCl and N_2O_5 on the surface of water droplets (Doren et al., 1999) and the uptake of N_2O_5 on the surface of $(NH_4)_2SO_4$ (Griffiths and Anthony Cox, 2009).

Uptake of amines on kaolinite is the result of the coupled processes of mass accommodation (gas-to-particle transfer) and reaction with the reactive sites (mainly Lewis acid) on the surface of kaolinite. Thus,

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_{\mathrm{rxn}}} \quad (11)$$

where α is the mass accommodation coefficient; Γ_{rxn} is the surface reaction resistance (Ammann et al., 2003). If the reaction on the surface is fast enough, accommodation at the surface of amines becomes the rate determining step (RDS) and γ is equal to α. According to the thermodynamic model of mass accommodation (Davidovits et al., 2006), the relationship between the α and temperature can be described as,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

$$\ln\frac{\alpha}{1-\alpha} = \ln\frac{\gamma}{1-\gamma} = \frac{-\Delta H_{obs}}{RT} + \frac{\Delta S_{obs}}{R} \quad (12)$$

where R is the ideal gas constant; T is reaction temperature. Therefore, the adsorption enthalpy (ΔH_{obs}) and entropy (ΔS_{obs}) for amines on kaolinite can be obtained by equation (12) (Liu et al., 2010b;Hudson et al., 2002;Davidovits et al., 2006). Figure 5 shows the plot of $\gamma/(1-\gamma)$ versus inverse temperature. The temperature dependence of the γ of amines on kaolinite is consistent with accommodation-controlled uptake with the assumption $\gamma=\alpha$. This also satisfactorily explained the independence of the observed uptake coefficient on sample mass as discussed in Section 3.2, because of the large γ.

The ΔH_{obs} and ΔS_{obs} for adsorption of MA on kaolinite were determined to be -7.8±0.8 kJ mol^{-1} and -77.1±3.2 J K^{-1} mol^{-1}, respectively. They were -9.9±2.9 kJ mol^{-1} and -84.1±11.8 J K^{-1} mol^{-1} for DMA and -9.4±1.0 kJ mol^{-1} and -80.6±3.7 J K^{-1} mol^{-1} for TMA. The ΔH_{obs} or ΔS_{obs} values are not significantly different at the 0.05 level among the different amines. The ΔH_{obs} for uptake of amines on kaolinite are comparable with that of carbonyl sulfide (-10.7±1.1 kJ mol^{-1}) on kaolinite (Liu et al., 2010b), while they are smaller than the ΔH_{obs} of N_2O_5 on $(NH_4)_2SO_4$ (-33 KJ mol^{-1}) (Griffiths and Anthony Cox, 2009) and N_2O_5 on sulfuric acid aerosol (-25 KJ mol^{-1}) (Hallquist et al., 2000). The relative small ΔH_{obs} values of amines on kaolinite demonstrate that amines weakly adsorb on kaolinite.

The empirical formulas relating γ_t of amines on kaolinite and temperature are given as

$$\gamma_{eff}(\mathrm{MA}) = \frac{\exp(938.8/T-9.3)}{1+\exp(938.8/T-9.3)} \quad (13)$$

$$\gamma_{eff}(\mathrm{DMA}) = \frac{\exp(1193.8/T-10.1)}{1+\exp(1193.8/T-9.3)} \quad (14)$$

$$\gamma_{eff}(\mathrm{TMA}) = \frac{\exp(1126.5/T-9.6)}{1+\exp(1126.5/T-9.6)} \quad (15)$$

Thus, the γ_t at other temperatures can be obtained using these equations.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

4 Conclusions and environmental implications

The uptake of amines on kaolinite was investigated within a temperature range of 232-300 K. It was found that Lewis acid sites on kaolinite were the main contributors to the uptake of amines. The initial effective uptake coefficients of amines were $(2.27\pm0.26)\times10^{-3}$, $(1.71\pm0.26)\times10^{-3}$ and $(2.95\pm0.63)\times10^{-3}$, respectively, for MA, DMA and TMA on kaolinite at 300 K. The basicity of amines was weakly correlated with the reactivity at 300 K, namely, TMA, with the strongest basicity, showed the highest reactivity on kaolinite, and vice versa for DMA. The uptake coefficients increased ~3-fold with decreasing temperature from 300 K to 232 K. Based on the temperature dependence of the uptake coefficients, the uptake of amines was predominantly ascribed to mass accommodation. The ΔH_{obs} of MA, DMA and TMA on kaolinite were -7.8 ±0.8, -9.9 ±2.9 and -9.4 ±1.0 kJ mol^{-1}, respectively. The corresponding ΔS_{obs} were -77.1±3.2, -84.1±11.8 and -80.6±3.7 J K^{-1} mol^{-1}. The empirical formula relating γ and temperature can be expressed as shown in Eqs. (13)-(15).

With the measured uptake coefficients, the lifetimes of amines attributable to uptake by kaolinite can be estimated by

$$\tau = \frac{4}{\gamma_{eff}\bar{v}SA} \quad (16)$$

where $\bar{v}$ is the average velocity of amines (m s^{-1}); γ_{eff} is the effective uptake coefficient at 300 K; and *SA* is the surface area of particles in the dust event (m^2 m^{-3}). If we assume that all mineral dust is in the form of kaolinite, and the dust loading is 150 μm^2 cm^{-3} (de Reus et al., 2000; Frinak et al., 2004) under extreme conditions, the lifetimes of MA, DMA and TMA due to heterogeneous uptake onto dust were estimated to be 7.2, 11.5 and 7.7 h, respectively. In the atmosphere, oxidation by OH was considered to be the main degradation pathway of amines. The second-order rate constants of aliphatic amines toward OH are $(2\text{-}6)\times10^{-11}$ cm^{-3} molecule^{-1} s^{-1} (Atkinson,

1986). Thus, their lifetimes are in the range of 4.6-13.8 h with the assumption of a 24 h average OH concentration of 1.0×10^{6} molecules cm^{-3} (Prinn et al., 2001). Therefore, the estimated lifetimes of amines related to heterogeneous uptake by mineral dust are comparable to those consumed by OH oxidation. Of course, the contribution of heterogeneous uptake to the amine sink might be overestimated here, because the uptake coefficient decreased with exposure time quickly as shown in Fig. 1. It should be noted that the γ_t values of amines on kaolinite increased significantly at low temperature as shown in Table 2. On the other hand, high concentrations of mineral dust are possible near particular emission sources, such as agriculture, which is an important source of amines (Kuhn et al., 2011). Therefore, mineral dust may have an important influence on the local concentration of amines, especially in low temperature regions with high concentrations of mineral dust. Finally, uptake experiments were performed in a Knudsen cell reactor in this study. Although water vapor was also introduced into the reactor along with amines, the RH was still lower than 1 %. If high RH can also promote the uptake of amines on mineral dust as observed on $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl (Chan and Chan, 2012), the contribution of mineral dust to the amine sink will be enhanced.

Recent studies have found that alkylaminium sulfates with lower vapor pressure than that of ammonium sulfate are more thermally stable than their counterparts (Lavi et al., 2013) and the displacement reactions of alkylamines with ammonium sulfate lead to a transition from the crystalline to an amorphous phase, improved water uptake (Qiu and Zhang, 2012) and CCN activity (Lavi et al., 2013), and less scattering ability for 360 and 420 nm radiation (Lavi et al., 2013). This means that heterogeneous reactions greatly modify the properties of aerosols (Gomez-Hernandez et al., 2016). Kaolinite particles have been confirmed as effective ice nuclei (IN) (Wex et al., 2014;Salam et al.,

2006), while physically adsorbed amines on kaolinite can reduce the water wettability of kaolinite (Kitahara and Williamson, 1964). This means that heterogeneous uptake of amines on kaolinite may have an influence on the IN ability of kaolinite, although this needs to be confirmed with experiments in the future.

Alkylaminium sulfate salts, even in freshly nucleated nanoparticles (lower than 10 nm in diameter), will not be likely to undergo particle to gas partitioning at room temperature because of their thermal stability and ultralow vapor pressures (Lavi et al., 2013). However, physical adsorption with small enthalpy takes place between amines and kaolinite. This means that adsorbed amines probably at or near the emission sources of amines can be transported with dust to other regions, and subsequently might undergo particle-to-gas partitioning in air with a lower concentration of amines, and subsequently, further participate in new particle formation with acids or displacement reactions with ammonium compounds. In this process, mineral dust takes on the role of a carrier or reservoir of amines.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (41275131) and the Strategic Priority Research Program of Chinese Academy of Sciences (XDB05040100, XDB05010300).

References:

Almeida, J., Schobesberger, S., Kurten, A., Ortega, I. K., Kupiainen-Maatta, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppa, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petaja, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J.,

Baltensperger, U., Worsnop, D. R., Vehkamaki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, Nature, 502, 359-363, doi: 10.1038/nature12663, 2013.
Ammann, M., Poschl, U., and Rudich, Y.: Effects of reversible adsorption and Langmuir-Hinshelwood surface reactions on gas uptake by atmospheric particles, Phys. Chem. Chem. Phys., 5, 351-356, doi: 10.1039/B208708A, 2003.
Atkinson, R.: Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions, Chem. Rev., 85, 69-201, doi: 10.1021/cr00071a004, 1986.
Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, doi:10.5194/acp-6-3625-2006, 2006.
Benvenutti, E. V., Gushikem, Y., and Davanzo, C. U.: Pyridine used as a probe for internal bronsted acid sites in pyrochlore antimony(v) oxide - an infrared-spectroscopy study, Appl. Spectrosc., 46, 1474-1476, doi: 10.1366/000370292789619179, 1992.
Brindley, G. W., and Robinson, K.: Structure of Kaolinite, Nature, 156, 661-662, doi:10.1038/156661b0, 1945.
Busca, G.: The surface acidity of solid oxides and its characterization by IR spectroscopic methods. An attempt at systematization, Phys. Chem. Chem. Phys., 1, 723-736, doi: 10.1039/A808366E, 1999.
Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Size-Dependent Reactions of Ammonium Bisulfate Clusters with Dimethylamine, J. Phys. Chem. A, 114, 11638-11644, doi: 10.1021/jp106363m, 2010a.
Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine exchange into ammonium bisulfate and ammonium nitrate nuclei, Atmos. Chem. Phys., 10, 3495-3503, doi: 10.5194/acp-10-3495-2010, 2010b.
Bzdek, B. R., Ridge, D. P., and Johnston, M. V.: Amine reactivity with charged sulfuric acid clusters, Atmos. Chem. Phys., 11, 8735-8743, doi:10.5194/acp-11-8735-2011, 2011.
Chan, L. P., and Chan, C. K.: Displacement of Ammonium from Aerosol Particles by Uptake of Triethylamine, Aerosol Sci.Technol., 46, 236-247, doi: 10.1080/02786826.2011.618815, 2012.
Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P., and Duce, R. A.: Organic nitrogen deposition on land and coastal environments: a review of methods and data, Atmos. Environ., 37, 2173-2191, doi: 10.1016/S1352-2310(03)00133-X, 2003.
Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates, Atmos. Chem. Phys., 10, 9059-9223, doi: 10.5194/acp-10-9059-2010, 2010.
Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T., and Worsnop, D. R.: Mass accommodation and chemical reactions at gas-liquid interfaces, Chem. Rev., 106, 1323-1354, doi: 10.1021/cr040366k, 2006.
De Haan, D. O., Tolbert, M. A., and Jimenez, J. L.: Atmospheric condensed-phase reactions of glyoxal with methylamine, Geophys. Res. Lett., 36, L11819, doi: 10.1029/2009gl037441, 2009.
Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J., and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res., 101, 22869-22889, doi: 10.1029/96JD01818, 1996.
Doren, J. M. V., Watson, L. R., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Temperature dependence of the uptake coefficients of nitric acid, hydrochloric acid and nitrogen oxide (N2O5) by water droplets, J. Phys. Chem., 39, 3265-3269, doi: 10.1021/j100371a009, 1999.
Durgaprasad, G., Sathyanarayana, D. N., and Patel, C. C.: Infrared Spectra and Normal Vibrations of N,N-Dimethylformamide and N,N-Dimethylthioformamide, Bull. Chem. Soc. Jpn., 44, 316-322, doi: 10.1246/bcsj.44.316, 1971.
El Zein, A., and Bedjanian, Y.: Reactive Uptake of HONO to TiO2 Surface: "Dark" Reaction, J. Phys. Chem. A., 116, 3665-3672, doi: 10.1021/jp300859w, 2012.
Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331-3345, doi: 10.5194/acp-9-3331-2009, 2009.
Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines - Part I. A review, Atmos. Environ., 45, 524-546, doi: 10.1016/j.atmosenv.2010.10.012, 2011.
Gomez-Hernandez, M., McKeown, M., Secrest, J., Marrero-Ortiz, W., Lavi, A., Rudich, Y., Collins, D. R., and Zhang, R.: Hygroscopic Characteristics of Alkylaminium Carboxylate Aerosols, Environ. Sci. Technol., 50, 2292-2300, doi: 10.1021/acs.est.5b04691, 2016.
Grassian, V. H.: Chemical Reactions of Nitrogen Oxides on the Surface of Oxide, Carbonate, Soot, and Mineral Dust Particles: Implications for the Chemical Balance of the Troposphere, J. Phys. Chem. A.,

106, 860-877, doi: 10.1021/jp012139h, 2002.
Griffiths, P. T., and Anthony Cox, R.: Temperature dependence of heterogeneous uptake of N2O5 by ammonium sulfate aerosol, Atmos. Sci. Lett., 10, 159-163, doi: 10.1002/asl.225, 2009.
H. K. Hall, J.: Correlation of the Base Strengths of Amines, J. Am. Chem. Soc., 79, 5441-5444, doi: 10.1021/ja01577a030, 1957.
Hallquist, M., Stewart, D. J., Jacob Baker, A., and Cox, R. A.: Hydrolysis of N2O5 on Submicron Sulfuric Acid Aerosols, J. Phys. Chem. A, 104, 3984-3990, doi: 10.1021/jp9939625, 2000.
Hanisch, F., and Crowley, J. N.: Ozone decomposition on Saharan dust: an experimental investigation, Atmos. Chem. Phys., 3, 119-130, doi: 10.5194/acp-3-119-2003, 2003.
Hoffman, R. C., Kaleuati, M. A., and Finlayson-Pitts, B. J.: Knudsen Cell Studies of the Reaction of Gaseous HNO3 with NaCl Using Less than a Single Layer of Particles at 298 K: A Modified Mechanism, J. Phys. Chem. A., 107, 7818-7826, doi: 10.1021/jp030611o, 2003.
Hudson, P. K., Shilling, J. E., Tolbert, M. A., and Toon, O. B.: Uptake of Nitric Acid on Ice at Tropospheric Temperatures: Implications for Cirrus Clouds, J. Phys. Chem. A., 106, 9874-9882, doi: 10.1021/jp020508j, 2002.
Jen, C. N., McMurry, P. H., and Hanson, D. R.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, J. Geophys. Res.- Atmos., 119, 2014JD021592, doi: 10.1002/2014JD021592, 2014.
Keene, W. C., Montag, J. A., Maben, J. R., Southwell, M., Leonard, J., Church, T. M., Moody, J. L., and Galloway, J. N.: Organic nitrogen in precipitation over Eastern North America, Atmos. Environ., 36, 4529-4540, doi: 10.1016/S1352-2310(02)00403-X, 2002.
Keyser, L. F., Moore, S. B., and Leu, M. T.: Surface reaction and pore diffusion in flow-tube reactors, J. Phys. Chem., 95, 5496-5502, doi: 10.1021/j100167a026, 1991.
Kitahara, A., and Williamson, W. O.: Wettability of kaolinite treated with ammonia, methylamine, ethylamine, or their corresponding cations, J. Am. Ceram. Soc., 47, 313-317, doi: 10.1111/j.1151-2916.1964.tb12991.x, 1964.
Kuhn, U., Sintermann, J., Spirig, C., Jocher, M., Ammann, C., and Neftel, A.: Basic biogenic aerosol precursors: Agricultural source attribution of volatile amines revised, Geophys. Res. Lett., 38, L16811, doi: 10.1029/2011gl047958, 2011.
Lavi, A., Bluvshtein, N., Segre, E., Segev, L., Flores, M., and Rudich, Y.: Thermochemical, Cloud Condensation Nucleation Ability, and Optical Properties of Alkyl Aminium Sulfate Aerosols, J. Phys. Chem. C, 117, 22412-22421, doi: 10.1021/jp403180s, 2013.
Lee, A. K. Y., Zhao, R., Li, R., Liggio, J., Li, S.-M., and Abbatt, J. P. D.: Formation of Light Absorbing Organo-Nitrogen Species from Evaporation of Droplets Containing Glyoxal and Ammonium Sulfate, Environ. Sci. Technol., 47, 12819-12826, doi: 10.1021/es402687w, 2013a.
Lee, H. J., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Excitation Emission Spectra and Fluorescence Quantum Yields for Fresh and Aged Biogenic Secondary Organic Aerosols, Environ. Sci. Technol., 47, 5763-5770, doi: 10.1021/es400644c, 2013b.
Lin, J.-L., Lin, Y.-C., Lin, B.-C., Lai, P.-C., Chien, T.-E., Li, S.-H., and Lin, Y.-F.: Adsorption and Reactions on TiO2: Comparison of N,N-Dimethylformamide and Dimethylamine, J. Phys. Chem. C, 118, 20291-20297, doi: 10.1021/jp5044859, 2014.
Liu, X., Zhang, Y., Han, W., Tang, A., Shen, J., Cui, Z., Vitousek, P., Erisman, J. W., Goulding, K., Christie, P., Fangmeier, A., and Zhang, F.: Enhanced nitrogen deposition over China, Nature, 494, 459-462, doi:10.1038/nature11917, 2013.
Liu, Y., He, H., and Mu, Y.: Heterogeneous reactivity of carbonyl sulfide on α-Al_2O_3 and γ-Al_2O_3, Atmos. Environ., 42, 960-969, doi: 10.1016/j.atmosenv.2007.10.007, 2008.
Liu, Y., He, H., and Ma, Q.: Temperature Dependence of the Heterogeneous Reaction of Carbonyl Sulfide on Magnesium Oxide, J. Phys. Chem. A, 112, 2820-2826, doi: 10.1021/jp711302r, 2008
Liu, Y., and He, H.: Experimental and Theoretical Study of Hydrogen Thiocarbonate for Heterogeneous Reaction of Carbonyl Sulfide on Magnesium Oxide, J. Phys. Chem. A, 113 3387-3394, doi: 10.1021/jp809887c, 2009
Liu, Y., Ma, J., and He, H.: Heterogeneous reactions of carbonyl sulfide on mineral oxides: mechanism and kinetics study, Atmos. Chem. Phys., 10, 10335-10344, doi: 10.5194/acp-10-10335-2010, 2010a.
Liu, Y., Ma, J., Liu, C., and He, H.: Heterogeneous uptake of carbonyl sulfide onto kaolinite within a temperature range of 220–330 K, J. Geophys. Res., 115(D24311), doi:10.1029/2010JD014778, 2010b.
Liu, Y., Han, C., Liu, C., Ma, J., Ma, Q., and He, H.: Differences in the reactivity of ammonium salts with methylamine, Atmos. Chem. Phys., 12, 4855-4865, doi: 10.5194/acp-12-4855-2012, 2012a.
Liu, Y., Ma, Q., and He, H.: Heterogeneous uptake of amines by citric acid and humid acid, Environ. Sci Technol., 46, 11112-11118, doi: 10.1021/es302414v, 2012b.
Liu, Y., Han, C., Ma, J., Bao, X., and He, H.: Influence of relative humidity on heterogeneous kinetics of

NO2 on kaolin and hematite, Phys. Chem. Chem. Phys., 17, 19424-19431, doi: 10.1039/C5CP02223A, 2015a.

Liu, Y., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation, Atmos. Chem. Phys., 15, 13569-13584, doi: 10.5194/acp-15-13569-2015, 2015b.

Lloyd, J. A., Heaton, K. J., and Johnston, M. V.: Reactive Uptake of Trimethylamine into Ammonium Nitrate Particles, J. Phys. Chem. A, 113, 4840-4843, doi: 10.1021/jp900634d, 2009.

Meunier, C. L., Gundale, M. J., Sanchez, I. S., and Liess, A.: Impact of nitrogen deposition on forest and lake food webs in nitrogen-limited environments, Glob. Change Biol., 22, 164-179, doi: 10.1111/gcb.12967, 2016.

Miranda-Trevino1, J. C., and Coles, C. A.: Kaolinite properties, structure and influence of metal retention on pH, Appl. Clay Sci., 23, 133-139, doi:10.1016/S0169-1317(03)00095-4, 2003.

Muñoz, M. S. S., and Rossi, M. J.: Heterogeneous reactions of HNO3 with flame soot generated under different combustion conditions. Reaction mechanism and kinetics, Phys. Chem. Chem. Phys., 4, 5110-5118, doi: 10.1039/b203912p, 2002.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C., and Seinfeld, J. H.: Secondary aerosol formation from atmospheric reactions of aliphatic amines, Atmos. Chem. Phys., 7, 2313-2337, doi:10.5194/acp-7-2313-2007, 2007.

Murphy, W. F., Zerbetto, F., Duncan, J. L., and McKean, D. C.: Vibrational spectrum and harmonic force field of trimethylamine, J. Phys. Chem., 97, 581-595, doi: 10.1021/j100105a010, 1993.

Ndour, M., D'Anna, B., George, C., Ka, O., Balkanski, Y., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of NO2 on mineral dust: Laboratory experiments and model simulations, Geophys. Res. Lett., 35, L05812, doi: 10.1029/2007gl032006, 2008.

Nguyen, T. B., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Brown carbon formation from ketoaldehydes of biogenic monoterpenes, Faraday Discuss., 165, 473-494, doi: 10.1039/C3FD00036B, 2013.

Nishino, N., Arquero, K. D., Dawson, M. L., and Finlayson-Pitts, B. J.: Infrared studies of the reaction of methanesulfonic acid with trimethylamine on surfaces, Environ. Sci. Technol., 48, 323-330, doi: 10.1021/es403845b, 2014.

Nunes, M. H. O., Silva, V. T. d., and Schmal, M.: The effect of copper loading on the acidity of Cu/HZSM-5 catalysts: IR of ammonia and methanol for methylamines synthesis, Appl. Catal. A: General, 294, 148-155, doi: 10.1016/j.apcata.2005.06.031, 2005.

Ongwandee, M., Morrison, G. C., Guo, X., and Chusuei, C. C.: Adsorption of trimethylamine on zirconium silicate and polyethylene powder surfaces, Colloid Surf. A: Physicochem. Eng. Asp., 310, 62-67, doi: 10.1016/j.colsurfa.2007.05.076, 2007.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Salameh, P., O'Doherty, S., Wang, R. H. J., Porter, L., and Miller, B. R.: Evidence for Substantial Variations of Atmospheric Hydroxyl Radicals in the Past Two Decades, Science, 292, 1882-1888, doi: 10.1126/science.1058673, 2001.

Qiu, C., Wang, L., Lal, V., Khalizov, A. F., and Zhang, R.: Heterogeneous Reactions of Alkylamines with Ammonium Sulfate and Ammonium Bisulfate, Environ. Sci. Technol., 45, 4748-4755, doi: 10.1021/es1043112, 2011.

Qiu, C., and Zhang, R.: Physiochemical Properties of Alkylaminium Sulfates: Hygroscopicity, Thermostability, and Density, Environ. Sci. Technol., 46, 4474-4480, doi: 10.1021/es3004377, 2012.

Qiu, C., and Zhang, R.: Multiphase chemistry of atmospheric amines, Phys. Chem. Chem. Phys., 15, 5738-5752, doi: 10.1039/c3cp43446j, 2013.

Salam, A., Lohmann, U., Crenna, B., Lesins, G., Klages, P., Rogers, D., Irani, R., MacGillivray, A., and Coffin, M.: Ice Nucleation Studies of Mineral Dust Particles with a New Continuous Flow Diffusion Chamber, Aerosol Sci.Technol., 40, 134-143, doi: 10.1080/02786820500444853, 2006.

Seisel, S., Lian, Y., Keil, T., Trukhin, M. E., and Zellner, R.: Kinetics of the interaction of water vapour with mineral dust and soot surfaces at T = 298 K, Phys. Chem. Chem. Phys., 6, 1926-1932, doi: 10.1039/B314568A, 2004.

Seisel, S., Bœrensen, C., Vogt, R., and Zellner, R.: Kinetics and mechanism of the uptake of N_2O_5 on mineral dust at 298K, Atmos. Chem. Phys., 5, 3423-3432, doi: 10.5194/acp-5-3423-2005, 2005.

Smith, I. W. M.: Laboratory Studies of Atmospheric Reactions at Low Temperatures, Chem. Rev., 103, 4549-4564, doi: 10.1021/cr020512r, 2003.

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., H.Scheckman, J., Williams, B. J., and McMurry, P. H.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, Proc. Natl. Acad. Sci. USA, 107, 6634-6639, doi: 10.1073/pnas.0912127107, 2010.

Tang, M. J., Thieser, J., Schuster, G., and Crowley, J. N.: Uptake of NO_3 and N_2O_5 to Saharan dust, ambient urban aerosol and soot: a relative rate study, Atmos. Chem. Phys., 10, 2965-2974, doi: 10.5194/acp-10-2965-2010, 2010.

Trainic, M., Riziq, A. A., Lavi, A., Flores, J. M., and Rudich, Y.: The optical, physical and chemical properties of the products of glyoxal uptake on ammonium sulfate seed aerosols, Atmos. Chem. Phys., 11, 9697-9707, doi: 10.5194/acp-11-9697-2011, 2011.

Underwood, G. M., Li, P., Al-Abadleh, H. A., and Grassian, V. H.: A Knudsen cell study of the heterogeneous reactivity of nitric acid on oxide and mineral dust particles, J. Phys. Chem. A, 105, 6609-6620, doi: 10.1021/jp002223h, 2001.

Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on Mineral Dust, Chem. Rev., 103, 4883-4939, doi: 10.1021/cr020657y, 2003.

van Breemen, N.: Nitrogen cycle: Natural organic tendency, Nature, 415, 381-382, doi: 10.1038/415381a, 2002.

Wang, L., Lal, V., Khalizov, A. F., and Zhang, R.: Heterogeneous Chemistry of Alkylamines with Sulfuric Acid: Implications for Atmospheric Formation of Alkylaminium Sulfates, Environ. Sci. Technol., 44 2461-2465, doi: 10.1021/es9036868, 2010a.

Wang, L., Wang, W., and Ge, M.: Heterogeneous uptake of NO2 on soils under variable temperature and relative humidity conditions, J. Environ. Sci., 24, 1759-1766, doi: 10.1016/S1001-0742(11)61015-2, 2012.

Wang, X. F., Gao, S., Yang, X., Chen, H., Chen, J. M., Zhuang, G. S., Surratt, J. D., Chan, M. N., and Seinfeld, J. H.: Evidence for High Molecular Weight Nitrogen-Containing Organic Salts in Urban Aerosols, Environ. Sci. Technol., 44, 4441-4446, doi: 10.1021/es1001117, 2010b.

Wex, H., DeMott, P. J., Tobo, Y., Hartmann, S., Rösch, M., Clauss, T., Tomsche, L., Niedermeier, D., and Stratmann, F.: Kaolinite particles as ice nuclei: learning from the use of different kaolinite samples and different coatings, Atmos. Chem. Phys., 14, 5529-5546, doi: 10.5194/acp-14-5529-2014, 2014.

Yu, G., Bayer, A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., and Keutsch, F. N.: Glyoxal in Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects, Environ. Sci. Technol., 45, 6336-6342, doi: 10.1021/es200989n, 2011.

Zarzana, K. J., De Haan, D. O., Freedman, M. A., Hasenkopf, C. A., and Tolbert, M. A.: Optical Properties of the Products of α-Dicarbonyl and Amine Reactions in Simulated Cloud Droplets, Environ. Sci. Technol., 46, 4845-4851, doi: 10.1021/es2040152, 2012.

Zhang, H. F., Ren, S. Y., Yu, J. W., and Yang, M.: Occurrence of selected aliphatic amines in source water of major cities in China, J. Environ. Sci., 24, 1885-1890, doi: 10.1016/s1001-0742(11)61055-3, 2012.

Zhang, Y., and Carmichael, G. R.: The Role of Mineral Aerosol in Tropospheric Chemistry in East Asia—A Model Study, Journal of Applied Meteorology, 38, 353-366, doi: 10.1175/1520-0450, 1999.

Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L., and Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China, Atmos. Chem. Phys., 15, 2031-2049, doi: 10.5194/acp-15-2031-2015, 2015.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Tables

Table 1. Comparison of the γ of amines on typical particles.

Amines	Particles	γ	T (K)	Ref.
MA	Kaolinite	$2.27 \pm 0.26 \times 10^{-3}$	300	This study
	Citric acid [a]	$7.31 \pm 1.13 \times 10^{-3}$	300	(Liu et al., 2012b)
	Humic acid [a]	$1.26 \pm 0.07 \times 10^{-5}$	300	(Liu et al., 2012b)
	$(NH_4)_2SO_4$ [a]	$6.30 \pm 1.03 \times 10^{-3}$	300	(Liu et al., 2012a)
	$(NH_4)_2SO_4$ [b]	$2.60\text{-}3.40 \times 10^{-2}$	293	(Qiu et al., 2011)
	NH_4HSO_4 [a]	$1.78 \pm 0.36 \times 10^{-2}$	300	(Liu et al., 2012a)
	NH_4NO_3 [a]	$8.79 \pm 1.99 \times 10^{-3}$	300	(Liu et al., 2012a)
	NH_4Cl [a]	$2.29 \pm 0.28 \times 10^{-3}$	300	(Liu et al., 2012a)
	62% H_2SO_4 solution	$2.00 \pm 0.20 \times 10^{-2}$	283	(Wang et al., 2010a)
	71% H_2SO_4 solution	$2.00 \pm 0.30 \times 10^{-2}$	283	(Wang et al., 2010a)
	82% H_2SO_4 solution	$3.00 \pm 0.50 \times 10^{-2}$	283	(Wang et al., 2010a)
DMA	Kaolinite	$1.71 \pm 0.26 \times 10^{-3}$	300	This study
	Citric acid [a]	$6.65 \pm 0.49 \times 10^{-3}$	300	(Liu et al., 2012b)
	Humic acid [a]	$7.33 \pm 0.40 \times 10^{-6}$	300	(Liu et al., 2012b)
	$(NH_4)_2SO_4$ [b]	$3.20\text{-}3.40 \times 10^{-2}$	293	(Qiu et al., 2011)
	$[(NH_4)_3(SO_4)_2]^+$ cluster [c]	0.85 ± 0.26	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_2(HSO_4)]^+$ cluster [c]	1.05 ± 0.26	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_3(HSO_4)_2]^+$ cluster [c]	0.85 ± 0.22	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_4(HSO_4)_3]^+$ cluster [c]	0.61 ± 0.15	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_3(NO_3)_2]^+$ cluster [c]	0.53 ± 0.21	r.t.	(Bzdek et al., 2010b)
	30% $(NH_4)_2SO_4$ solution	$1.80\text{-}0.60 \times 10^{-2}$	293	(Qiu et al., 2011)
	62% H_2SO_4 solution	$3.00 \pm 0.60 \times 10^{-2}$	283	(Wang et al., 2010a)
	71% H_2SO_4 solution	$2.50 \pm 0.40 \times 10^{-2}$	283	(Wang et al., 2010a)
	82% H_2SO_4 solution	$3.20 \pm 0.30 \times 10^{-2}$	283	(Wang et al., 2010a)
TMA	Kaolinite	$2.95 \pm 0.63 \times 10^{-3}$	300	This study
	Citric acid [a]	$5.82 \pm 0.68 \times 10^{-3}$	300	(Liu et al., 2012b)
	Humic acid [a]	$4.75 \pm 0.15 \times 10^{-6}$	300	(Liu et al., 2012b)
	$(NH_4)_2SO_4$ [b]	$2.40\text{-}2.90 \times 10^{-2}$	293	(Qiu et al., 2011)
	$[(NH_4)_2(HSO_4)]^+$ cluster [c]	0.90 ± 0.26	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_3(HSO_4)_2]^+$ cluster [c]	0.66 ± 0.26	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_4(HSO_4)_3]^+$ cluster [c]	0.64 ± 0.26	r.t.	(Bzdek et al., 2010b)
	$[(NH_4)_3(NO_3)_2]^+$ cluster [c]	0.40 ± 0.12	r.t.	(Bzdek et al., 2010b)
	NH_4NO_3 [d]	$2.00 \pm 2.00 \times 10^{-3}$	r.t.	(Lloyd et al., 2009)
	62% H_2SO_4 solution	$2.20 \pm 0.20 \times 10^{-2}$	283	(Wang et al., 2010a)
	71% H_2SO_4 solution	$2.70 \pm 0.80 \times 10^{-2}$	283	(Wang et al., 2010a)
	82% H_2SO_4 solution	$3.50 \pm 0.20 \times 10^{-2}$	283	(Wang et al., 2010a)

Note: Note: [a] coarse particles (grounded crystalline); [b] coarse particles (crystalline or amorphous from solution); [c] 1-2 nm particles; [d] 20-500 nm particles

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Table 2. The γ_{eff} of amines on kaolinite in the temperature range 232-300 K

Temperature (K)	γ_{eff} (MA)	γ_{eff} (DMA)	γ_{eff} (TMA)
232	$5.79 \pm 0.64 \times 10^{-3}$	$6.04 \pm 1.24 \times 10^{-3}$	$9.24 \pm 0.26 \times 10^{-3}$
237	$4.70 \pm 0.58 \times 10^{-3}$	-	-
248	$3.90 \pm 0.86 \times 10^{-3}$	$5.35 \pm 1.03 \times 10^{-3}$	$5.90 \pm 0.93 \times 10^{-3}$
258	-	-	$4.40 \pm 0.03 \times 10^{-3}$
263	$3.51 \pm 0.39 \times 10^{-3}$	$4.68 \pm 1.23 \times 10^{-3}$	-
278	$2.63 \pm 0.30 \times 10^{-3}$	$2.25 \pm 0.46 \times 10^{-3}$	$3.44 \pm 0.40 \times 10^{-3}$
300	$2.27 \pm 0.26 \times 10^{-3}$	$1.71 \pm 0.26 \times 10^{-3}$	$2.95 \pm 0.63 \times 10^{-3}$

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Figure captions

Figure 1. Uptake curves and the corresponding uptake coefficient of amines on kaolinite at 300 K. The sample mass was 19.3, 20.6 and 20.2 mg, respectively.

Figure 2. *In situ* FTIR spectra of amines adsorbed on kaolinite for 30 min at 300 K. The IR spectra were recorded taking the dried kaolinite as reference.

Figure 3. Mass dependence of γ_{obs} for amines on kaolinite at 300 K. Error bars indicate 1 σ for repeated experiments.

Figure 4. (A) Box chart for the γ_{eff} of amines on kaolinite measured at 300 K. (B) Relationship between the γ_{eff} and the basicity of amines.

Figure 5. Temperature dependence of γ_{eff} for amines on kaolinite.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

Figures

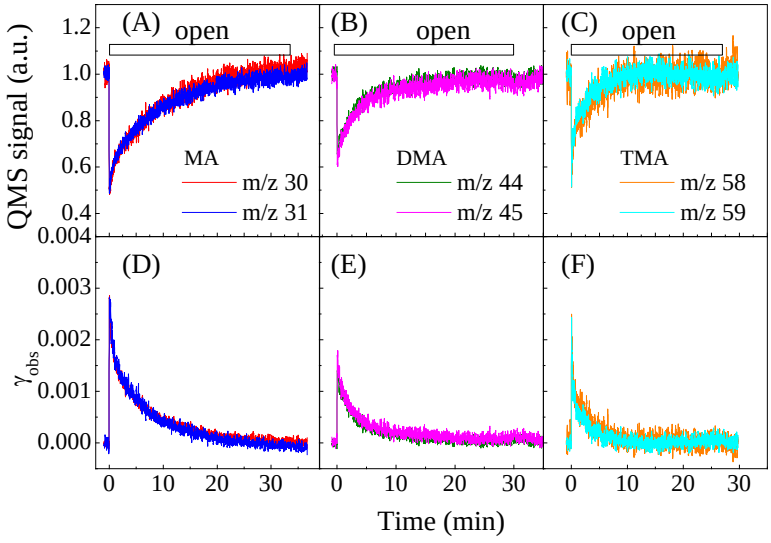

Fig. 1

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

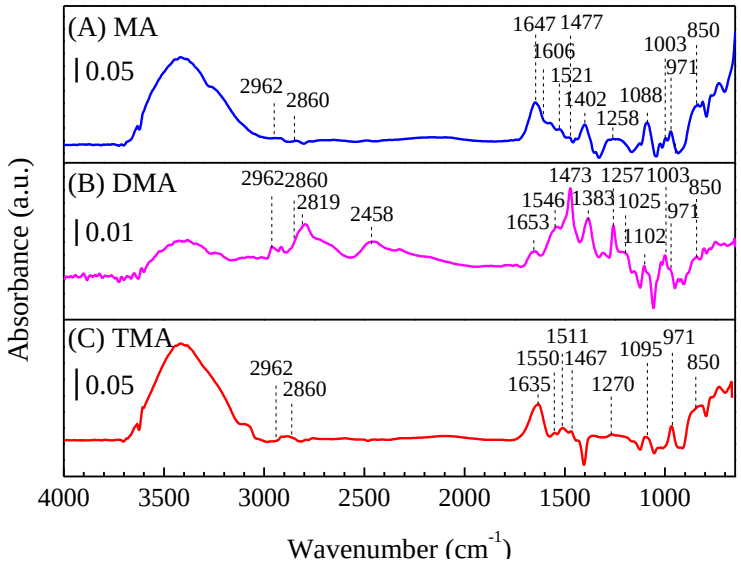

Fig. 2

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

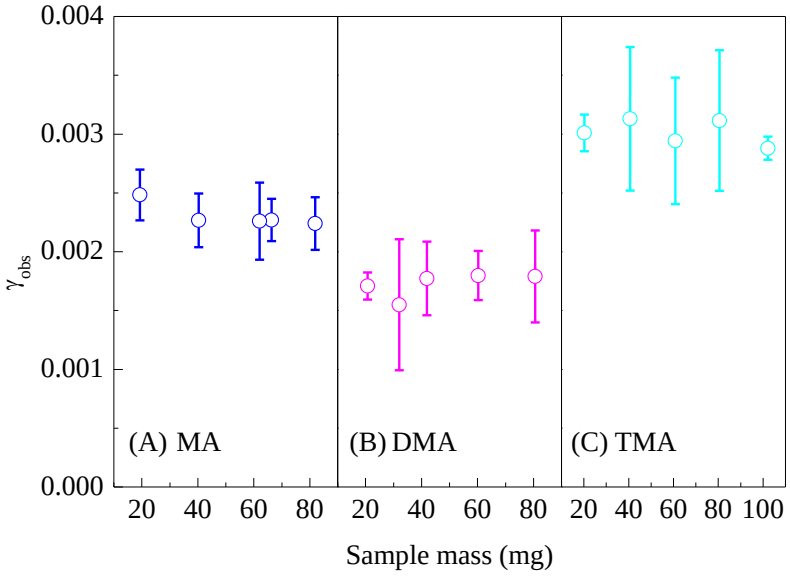

Fig. 3

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

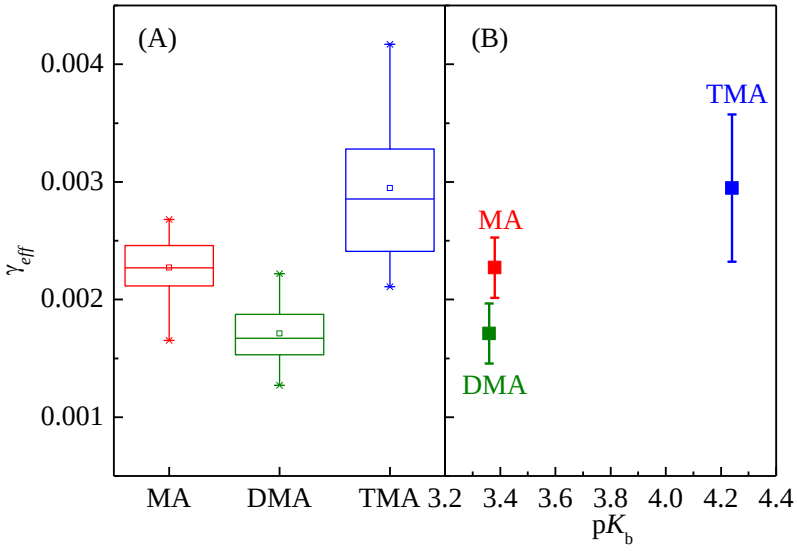

Fig. 4

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-538, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 23 June 2016

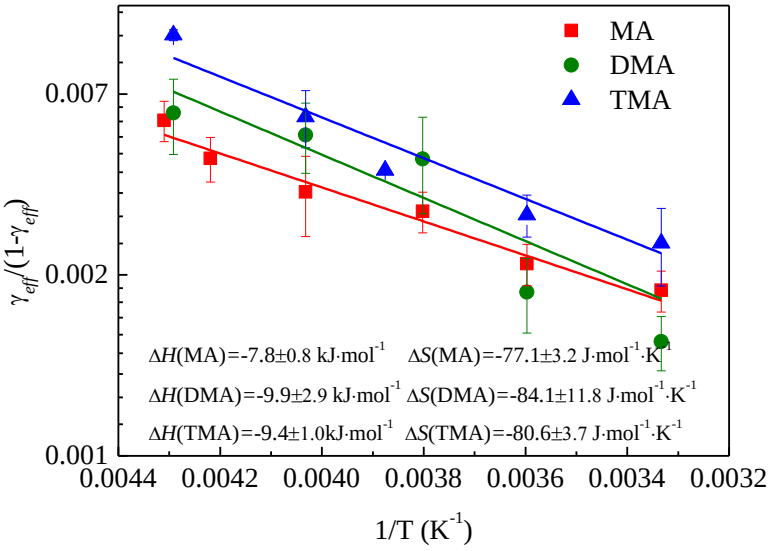

Fig. 5