An Experimental and Theoretical Assessment of the Dissociation of Ammonium Nitrate Aerosol

Talbot, Nicholas
2014

AN EXPERIMENTAL AND THEORETICAL ASSESSMENT OF THE DISSOCIATION OF AMMONIUM NITRATE AEROSOL

Nicholas TALBOT, Vladimír ŽDÍMAL, Jakub ONDRÁČEK, Jaroslav SCHWARZ

Laboratory of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals of the ASCR, v.v.i., Rozvojová 2, 165 02 Prague 6 - Suchdol, Czech Republic.

Key words: Ammonium Nitrate, Dissociation, Shrinking rate, Modeling.

INTRODUCTION

Secondary inorganic aerosol makes up a sizable fraction of total aerosol loading in the northern hemisphere, where ammonium nitrate is found to contribute upto 30% of the fine fraction (Dassios and Pandis, 1998).

Previous studies show that once indoors, ammonium nitrate concentrations are much lower than would be predicted based solely on deposition and penetration losses (Lunden et al, 2003). Other papers have noted the strong association between the dissociation rates of ammonium nitrate and temperature (Stelson and Seinfeld, 1982, Wexler and Seinfeld, 1990).

Previous research have used thermodynamic models to obtain dissociation rates. However modeled predictions are generally much faster than those experimentally observed, implying the existence of some form of kinetic restraint. (Hightower and Richardson, 1988, Lawson and Taylor, 1983). Moreover, very few research groups have coupled both experimental observations and theoretical modelling to try to gain a greater understanding of the processes governing the dissociation rate.

This paper seeks to address this imbalance by deploying both experimental observations with a kinetics driven model to further investigate dissociation rates and offer greater insight into ammonium nitrate dissociation behaviour.

EXPERIMENTAL SETUP

The dissociation kinetics of ammonium nitrate was investigated experimentally utilizing a tandem differential mobility analyzer/scanning mobility particle sizer system (Dassios and Pandis, 1998). Monodisperse aerosol of ammonium nitrate has been produced by nebulizing 1 g/l ammonium nitrate solution, drying the polydisperse particles, bringing them to Boltzmann charge equilibrium using a Kr85 aerosol neutralizer, and selecting one mobility fraction in the Vienna type DMA.

The aerosol generation system was located in a thermally insulated box kept at controlled temperature below 10 °C. The monodisperse aerosol was then diluted by mixing it with a dry, particle-free air and fed into a laminar flow reactor in which temperature, relative humidity and flow rates were controlled.

Particle size distributions both upstream and downstream of the reactor were determined by an SMPS, consisting of a TSI EC 3080 provided with a long DMA, and a TSI CPC 3775. The stability of the aerosol generating system was further checked by the UCPC 3025A monitoring continuously the total particle concentrations

In the series of dissociation experiments, we studied the size changes of the ammonium nitrate aerosol for three selected particle sizes (50, 100 and 200 nanometres), at four reactor temperatures (15, 20, 25, and 30 °C), and several flow rates (between 0.6 to 1.6 l/min in 0.2 litre increments).
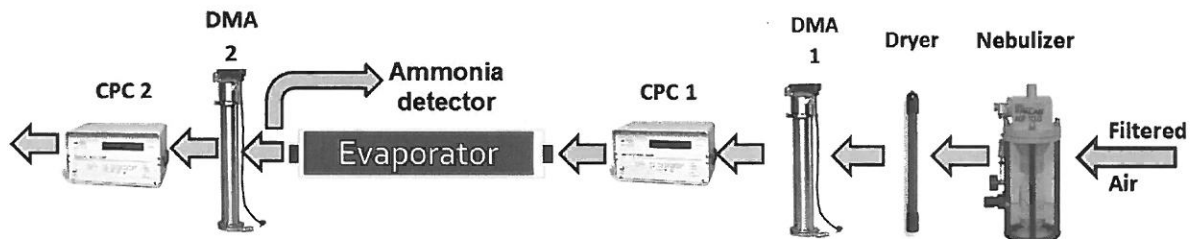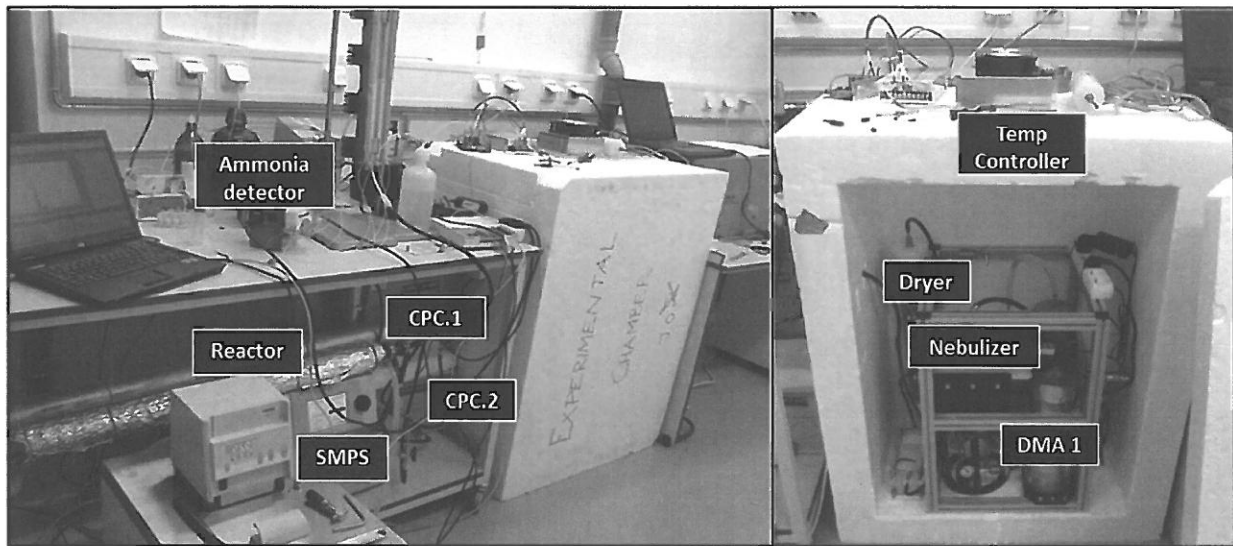

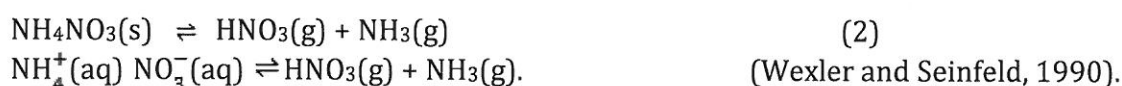**Fig 1**: Experimental design

THEORETICAL MODELLING

The observed changes of particle size were compared to the predictions of a mathematical model taking into account the ammonium nitrate dissociation kinetics, Kelvin effect and diffusion of ammonia and nitric acid from the particle to the bulk phase taking into account the measured concentration of ammonia gas in the bulk phase (equation 1).

$$\frac{d(dp)}{dt} = \frac{4DvM}{RPpdp} \left(\frac{P\infty}{T\infty} - \frac{Pd}{Td} \right) \phi \tag{1}$$

Where change in particle size over time takes into account diffusivity of the species (Dv) and molar mass (M) over gas constant (R), particle density (Pp) and size (dp). The driving force controlling the growth or shrinking of the particle is the partial pressure of the species well away from the particle surface, $P\infty$, minus the partial pressure of the species directly surrounding the particle Pd. The model assumed evaporation in the continuum regime using the Fuchs-Sutugin correction term, ϕ (Hinds, 1999).

RESULTS AND CONCLUSIONS

Experimental results indicate a strong association between increasing temperature and accelerated dissociation, tilting the reversible reactions shown in equation 2 below to the right hand side.

$$NH_4NO_3(s) \rightleftharpoons HNO_3(g) + NH_3(g) \tag{2}$$
$$NH_4^+(aq)\ NO_3^-(aq) \rightleftharpoons HNO_3(g) + NH_3(g). \qquad \text{(Wexler and Seinfeld, 1990).}$$

The shrinking rate shown in Figure 2(a) are indicative of the rate of evaporation of the precursor gases off the particle surface into the bulk phase. Adjusting the flow rates changes the residence times within the reactor allowing for observations of equilibrium stability through timescales of interest. To allow for the possibility of further drying of the particle once leaving the cutting DMA, samples were taken for each profile in-front of the reactor.

The changes in size recorded during these samples were then subtracted from the final size distribution, thus using the unevaporated sample as a calibration.
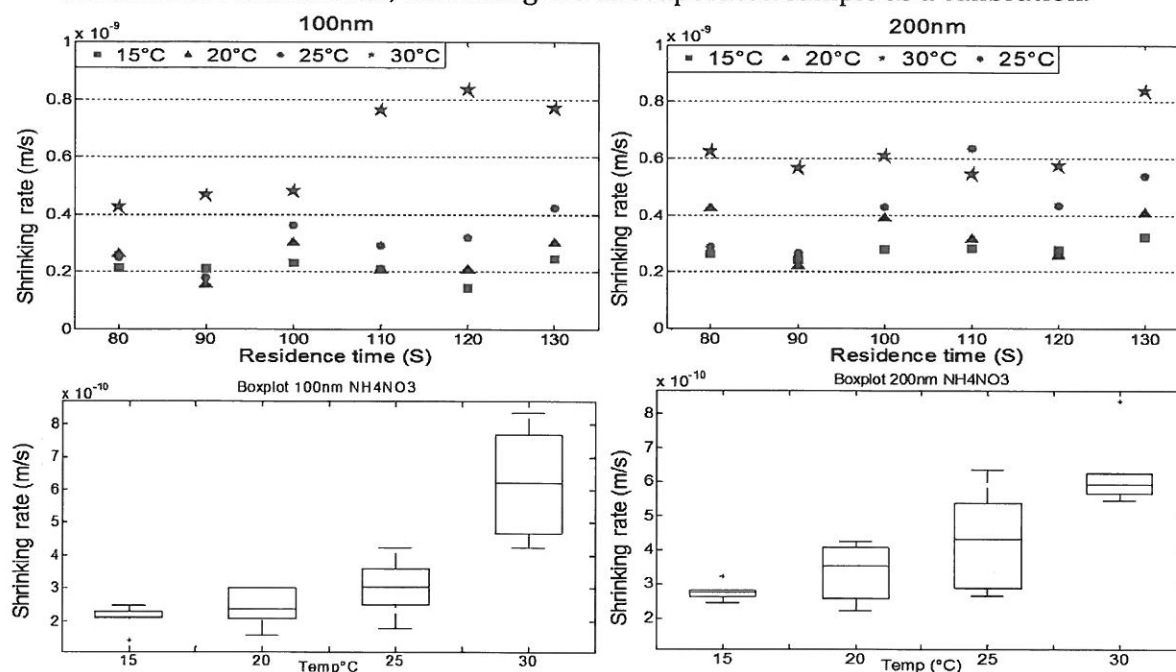

Fig: 2(a) (top): Evaporation rates of ammonium nitrate as a product of residence time and temperature. 2(b) shows boxplots and whiskers for the same data, showing the spread of data considering all residence times as a product of the temperature profile investigated.

The boxplots in figure 2(b) illustrates the distribution of data for each temperature profile considering all residence times. It is evident that for 15°C there is minimal spread in the shrinking rates throughout the residence time profiles. This indicates that the mass transfer within the reactor reached equilibrium. For 25°C and 30°C the spread in shrinking rate is far greater, indicating mass transfer processes had not yet reached the equilibrium.

Modeled results show the expected rates of dissociation to be more rapid than observed experimentally. This indicates the possible presence of a chemical or kinetic restraint. Whilst this is in line with findings from previous literature, the driving forces behind this are not fully understood. This presentation will further discuss these findings highlighting possible processes governing observed dissociation on ammonium nitrate.

ACKNOWLEDGMEMENTS

REFERENCES

Dassios, K.G and Pandis. S.N, 1998. The mass accommodation coefficient of Ammonium Nitrate aerosol. Atmospheric Environment. **33**, pp2993-3003.

Hinds W C, 1999. Aerosol Technology, Properties, Behavior and Measurements of Airborne Particles. Wiley publications, New York.

Larson T V, Taylor G S. 1983. On the evaporation of Ammonium Nitrate aerosol. *Atmospheric Environment.* **12**, pp2489-2495.

Lunden, M M, Revzan K L, Fischer M L, Thatcher T L, Littlejohn D, Hering S V, Brown N J. 2003. The transformation of outdoor ammonium nitrate aerosols in the indoor environment. *Atmospheric Environment.* **37**, pp5633-5644.

Richardson C B, Hightower R L. 1987. Evaportaion of Ammonium Nitrate particles, *Atmospheric Environment.* **33**, pp2993-3003.

Stelson, A W and Seinfeld J H, 1982, Relative humidity and temperature dependence of the Ammonium Nitrate dissociation constant. *Atmospheric Environment.* **16**, pp983-992.

Wexler, A.S., Seinfeld, J.H., 1990. The distribution of Ammonium salts among a size and composition dispersed aerosol, Atmospheric Environment. **24**, pp12331- 12 346.