An experimental and theoretical assessment of the dissociation of ammonium nitrate aerosol.

Nicholas Talbot, Vladimir Zdimal, Jakub Ondracek, 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.

Keywords: Ammonium Nitrate, Dissociation, Experiments, Modelling.

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 was produced by nebulizing 1g/ltr 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.

![Experimental setup](image)

Fig. 1: Experimental setup.

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 200nm), at four reactor temperatures (15, 20, 25, and 30˚C), and several flow rates (between 0.6 to 1.6 litres per minute in 0.2 litre increments).

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).

\[
\frac{d(d_p)}{dt} = \frac{4D_v M_p}{R P_d p_d \phi} \left( \frac{P_{\infty}}{T_{\infty}} - \frac{P_d}{T_d} \right)
\]

The model assumed evaporation in the continuum regime using the Fuchs-Sutugin correction term (Hinds, 1999).

Observed 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.

\[
\begin{align*}
\text{NH}_4\text{NO}_3(s) & \rightleftharpoons \text{HNO}_3(g) + \text{NH}_3(g) \\
\text{NH}_4^+(aq) \text{NO}_3^-(aq) & \rightleftharpoons \text{HNO}_3(g) + \text{NH}_3(g).
\end{align*}
\]

Results also indicate that NH4NO3 is most likely not completely dehydrated by the time it reaches the reactor. Therefore is likely further drying takes place in the reactor, helping explain in part the accelerated shrinking rates of the larger 200nm particles.

Shrinking and dissociation rates show a susceptibility to Kelvin surface / kinetics regime change effects when dp approaches 50nm. This is highlighted by a marked acceleration in dissociation behavior as the particle shrinks and is observed in both our dissociation rates and our modelled results.

The authors acknowledge support of this work by European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 315760 HEXACOMM.

References.
