

# Chemical ionization of clusters formed from sulfuric acid and dimethylamine or diamines

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Chemical ionization (CI) mass spectrometers are used to study atmospheric nucleation by detecting clusters produced by reactions of sulfuric acid and various basic gases. These instruments typically use nitrate to deprotonate and thus chemically ionize the clusters. In this study, we compare cluster concentrations measured using either nitrate or acetate. Clusters were formed in a flow reactor from vapors of sulfuric acid and dimethylamine, ethylene diamine, tetramethylethylene diamine, or butanediamine (also known as putrescine) (Jen et al. (2014) and (2016)).

These comparisons show that nitrate only chemically ionizes a small fraction of trimer and larger clusters in both the DMA and diamine with sulfuric acid systems. Measurements suggest that the more chemically neutral clusters are not chemically ionized by nitrate but are by acetate. In addition, acetate and nitrate CI measurements of sulfuric acid+DMA clusters generally agree with the qualitative trends of neutral and ion cluster predicted from computational chemistry (Ortega et al., 2012; Ortega et al., 2014). However, these measurements suggest that  $A_3^- \cdot B$  decomposes into  $A_2^-$  and  $A_1 \cdot B$ . Nitrate measurements of  $A_3^- \cdot B$  and  $A_4^- \cdot B$  show that these ions decompose at roughly the same time scales as the CI reaction time at room temperature.

In addition to reagent ion comparisons, we vary the ion-molecule reaction time to probe ion processes which include proton-transfer, ion-molecule clustering, and decomposition of ions. A model was developed to better identify the cluster types that are not efficiently deprotonated by nitrate and encompasses the neutral and ion cluster formation pathways. Comparison of model and measured cluster signals indicate that sulfuric acid dimer with two diamines are not efficiently chemical ionized by nitrate. Also model shows that in an acid-rich environment where  $[B]/[A_1] < 1$ ,  $A_2^-$  and  $A_3^-$  are primarily produced via ion-induced clustering pathways and contribute negligible amounts to overall dimer and trimer signals when any of these bases are present and at our 18 ms CI reaction time.

Ion decomposition upon deprotonation by acetate/nitrate was observed. However, more studies are needed to quantify to what extent ion decomposition affects observed cluster content and concentrations, especially those chemically ionized with acetate since it deprotonates more types of clusters than nitrate.

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