Explaining the Increased Sulfate Aerosol Formation Rates in Mixed Ammonia-Dimethylamine Systems

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Composed of gas phase molecules found in the atmosphere, aerosols form through a nucleation process before serving as cloud condensation nuclei (CCNs) that seed clouds. Aerosols have been found to have a net cooling effect on the global climate, but the process of their formation is still not well-understood.

Acid-base reactions between sulfuric acid [H_2SO_4, S] and ammonia [NH_3, A] promote aerosol formation and the effect is even greater for amines. Recent studies have shown that reactions between acids and stronger bases, such as amines, may further enhance aerosol formation by preventing evaporation. Furthermore, the presence of ammonia and amines increases aerosol formation rates significantly more than ammonia or an amine alone. For this study, dimethylamine [$(CH_3)_2NH$, DMA] was chosen due to its stronger basicity and larger size. The possible configurations of $(H_2SO4)_2$-$((CH_3)_2NH)$-(NH_3) and $(H_2SO4)_2$-$((CH_3)_2NH)_2$ were sampled using a genetic algorithm applied on semi-empirical (PM7, SCC-DFTB) potential energy surfaces. The low energy structures were subject to quantum mechanical calculations such as PW91, M06-2X, and wB97X-D with 6-311++G** basis set. From our data, we have come to the conclusion that binding energies strongly correlate with the basicity of the base: S_2-DMA_2 > S_2-DMA-A > S_2-A_2. These conclusions disagree with experimental nucleation rates which increase in the order S_2-DMA-A > S_2-DMA-DMA > S_2-A_2. The reason for these discrepancies are explored.

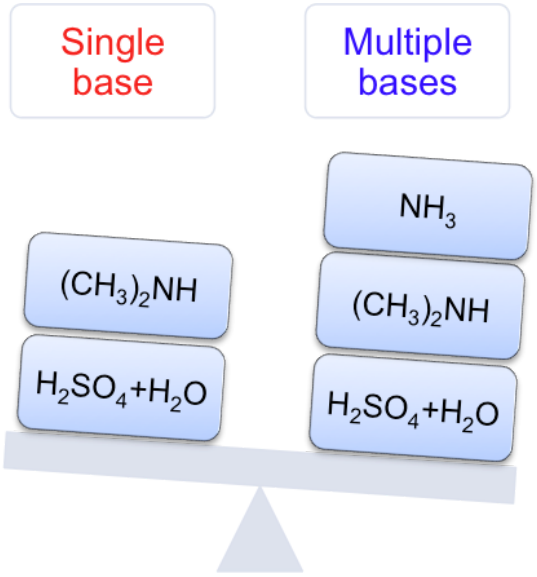

Figure 1: How does the presence of two different bases enhance aerosol formation rates compared to single base systems?