

Impacts of acidity on multiphase chemistry of organic acids in aqueous particles and clouds

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The acidity of aqueous atmospheric solutions is a key parameter driving both partitioning of semi-volatile acidic or basic trace gases and their linked aqueous-phase chemistry. On the other hand, acidity of atmospheric aqueous phases, e.g. deliquesced aerosol particles, cloud and fog droplets, is conversely affected by aqueous-phase chemistry processes. Those feedbacks in acidity and chemistry have crucial implications for the (i) tropospheric lifetime of air pollutants, hence air quality and atmospheric aerosol composition, (ii) deposition input into other terrestrial and oceanic ecosystems, (iii) the visibility, (iv) climate and (v) human health. Due to their fundamental role, atmospheric research has gained substantial progress in the understanding in feedbacks of acidity and multiphase chemistry. In the present study, the current state of knowledge on the acidity-multiphase chemistry feedbacks has been summarized. From a wide range of topics, two selected issues focusing on impacts of acidity (i) on the hydration of organic carbonyl compounds and (ii) multiphase chemistry of dissociating organic compounds in aqueous particles and clouds will be presented.

Hydration processes are typically known to be acid- or base-catalyzed. Thus, the acidity of an aqueous solution can affect the hydration and all other processes linked to it. This comprehensive literature study revealed that the hydration of simple aldehydes and ketones as well as dicarbonyls is less affected by acidity. However, for multifunctional carbonyl compounds such as pyruvic acid, the hydration equilibrium constant of the carbonyl group is strongly influenced by the electronic effects of the adjacent group. The hydration of carbonyl groups in compounds that also contain pH sensitive moieties, such as α -oxocarboxylic acids, is highly influenced by the acidity of the surrounding environment. However, this acidity effect is often not considered in multiphase models.

Furthermore, oxidation reactions of dissociating organic compounds can be affected by acidity. To examine the effect of acidity on the chemical processing of dissociating organic compounds, kinetic data for their oxidation by OH, NO₃ and O₃ have been newly compiled in the present study. Kinetic reactivity data of both protonated and deprotonated organic compounds together with their reactivity ratio κ_R have been investigated to identify possible acidity effects. The present study showed that, for OH reactions, the impact of acidity on the chemical kinetics is often quite small and only important for some specific compounds. On the other hand, for NO₃ reaction, particularly under cloud conditions, acidity can substantially affect the chemical NO₃-initiated processing of organic compounds. Less acidic conditions will enhance the degradation of dissociating compounds via NO₃ because of more rapid oxidation and possibility of additional ETR pathway. Furthermore, the present O₃ kinetic data analyses have demonstrated the role of acidity for ozonolysis processes, especially for phenolic compounds. Overall, the present study summarizes atmospheric implications and needs for future investigations, particularly with respect to changing aerosol and cloud acidity conditions in the future.