

Reactive Uptake of Glyoxal by Methylaminium-Containing Salts as a Function of Relative Humidity

Beatrix Rosette Mabato, Masao Gen, Yangxi Chu, and Chak Chan

City University of Hong Kong, School of Energy and Environment, Hong Kong, Hong Kong (brgmabato2-c@my.cityu.edu.hk)

Aqueous-phase reactions between glyoxal (Gly) and methylaminium salts have been proposed to produce brown carbon (BrC). Yet, studies on their heterogeneous reactions and the effect of relative humidity (RH) on BrC formation are scarce. Here, we report the reactive uptake of Gly by methylaminium chloride, sulfate, and nitrate (MeACl, MeAS, and MeAN, respectively) particles as a function of RH using in situ Raman/fluorescence spectroscopy. Bulk-phase reactions of premixed solutions of Gly and methylaminium salt were also examined using UV/vis spectroscopy. Results of bulk-phase reactions show that the first-order reaction rate constants of BrC formation are about $7.0 \times 10^{-7} \text{ s}^{-1}$ regardless of salt type. For the particle-phase reactions, in situ Raman analysis, which was limited to MeAS and MeAN particles due to the Raman-inactive Cl anion of MeACl, yielded the first-order rate constants of BrC formation based on the fluorescence emissions from BrC. Similar to the bulk-phase reactions, the estimated particle-phase first-order reaction rate constants of MeAS and MeAN particles are comparable as indicated by the comparable effective Henry's law constants of Gly in the two salt particles at a particular RH. The particle-phase rate constants increase from 8.6×10^{-6} to $1.0 \times 10^{-4} \text{ s}^{-1}$ for MeAS and from 1.0×10^{-5} to $7.2 \times 10^{-5} \text{ s}^{-1}$ for MeAN when RH decreases from 80 to 30%. They are higher than the bulk-phase values, likely due to the "salting-in" effect at higher salt concentrations. The "salting-in" effect can explain the enhanced formation of BrC with decreasing RH. In contrast to the reactions between Gly and ammonium salts (Environ. Sci. Technol. 2018, 52, 6903-6911), the promoted dehydration reactions do not play a significant role in the enhanced BrC formation likely due to the higher hygroscopicity of methylaminium salts.