Anion-catalyzed NO2 dissolution on aqueous microdroplets: A new source of HONO?

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NO_X have been recognized as crucial components of photochemical smog, while atmospheric chemical models still fail to correctly predict OH/HO concentrations under NO_X-rich conditions [Kanaya et al. JGR 2008, 113, D06301]. This deficiency may be due, in part, to the still uncertain rates and mechanism for the reactive dissolution of NO_2 ($2NO_2 + H_2O = NO_3^- + H^+ + HONO$) in fog and aerosol droplets. Here we report experiments in which *in situ* ion production on the surface of aqueous microdroplets exposed to NO_2(g) for ˜1 ms is monitored by nebulizer-assisted online electrospray mass spectrometry [Enami et al. JPCA 2007, 111, 13032]. NO_2 does not dissolve in deionized pure water (product ion signals below detection limit) but readily yields NO_3^- on aqueous NaX (X = Cl, Br, I) microdroplets. NO_3^- signals vary non-monotonically with electrolyte concentration yielding peak NO_2 uptake coefficients $gamma_{max}$ ˜10^{-4} at [NaX] ˜1 mM that are 10^3 larger than in neat water. By showing that gamma is strongly modulated by electrolyte content, these results seem to resolve outstanding discrepancies between previous measurements in neat water vs. NaCl-seeded clouds. In order to reveal the detail mechanism, the generation of NO_3^- in various aqueous dicarboxylic acids microdroplets over the pH range from 3 to 9 has been studied further. We found the evidences of the H^+/NO_3^-/HONO(g) formations during the short (˜1 ms) NO_2(g) exposure on the dicarboxylic acids microdroplets surfaces. Our reaction mechanism suggests that atmospheric HONO(g) emission may be controlled by electrolyte concentrations in fogs/clouds/aerosols droplets. Therefore, time dependent ionic composition as well as specific surface areas of fogs/clouds/aerosols is required to model these processes. Further atmospheric implications will be discussed.