

Atmospheric aqueous phase T- and pH-dependent OH_(aq) radical reaction kinetics with glycine, alanine, serine and threonine

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Amino acids are substances of central importance in biological activities and can be emitted into the atmosphere as constituents of primary aerosol particles. For example, glycine, alanine, serine and threonine are four amino acids which could be oxidized by hydroxyl radical (OH) in the aqueous phase of atmospheric aerosol particles and droplets. Within the present study, the OH radical reaction kinetics of the four amino acids were investigated by a laser flash photolysis-long path absorption setup using the competition kinetics method under temperature and pH controls. Based on speciation calculations, the OH radical reaction rate constants of the fully protonated (H₂A⁺) and neutral (HA[±]) form were determined. The following T-dependent Arrhenius expressions were derived for the OH radical reactions with glycine, $k(T, \text{H}_2\text{A}^+) = (9.1 \pm 0.3) \times 10^9 \times \exp[(-2360 \pm 230 \text{ K})/T]$, $k(T, \text{HA}^\pm) = (1.3 \pm 0.1) \times 10^{10} \times \exp[(-2040 \pm 240 \text{ K})/T]$; alanine, $k(T, \text{H}_2\text{A}^+) = (1.0 \pm 0.1) \times 10^9 \times \exp[(-1030 \pm 340 \text{ K})/T]$, $k(T, \text{HA}^\pm) = (6.8 \pm 0.4) \times 10^{10} \times \exp[(-2020 \pm 370 \text{ K})/T]$; serine, $k(T, \text{H}_2\text{A}^+) = (1.1 \pm 0.1) \times 10^9 \times \exp[(-470 \pm 150 \text{ K})/T]$, $k(T, \text{HA}^\pm) = (3.9 \pm 0.1) \times 10^9 \times \exp[(-720 \pm 130 \text{ K})/T]$; and threonine, $k(T, \text{H}_2\text{A}^+) = (5.0 \pm 0.1) \times 10^{10} \times \exp[(-1500 \pm 100 \text{ K})/T]$, $k(T, \text{HA}^\pm) = (3.3 \pm 0.1) \times 10^{10} \times \exp[(-1320 \pm 90 \text{ K})/T]$ (in units of L mol⁻¹ s⁻¹).

The energy barriers (E_{Barrier}) of the OH radical induced H-atom abstractions were calculated by density functional theory performed with GAUSSIAN. According to the calculation results, amino and carboxyl group can increase the E_{Barrier} on neighboring C-atom, thus decrease the OH radical reaction rates. Hydroxide and methyl group can reduce the E_{Barrier} on neighboring C-atom, therefore increase the OH radical reactivity. The E_{Barrier} on the methyl group are close to those on neighboring C-atom, suggesting similar H-atom abstraction opportunities on both, further increasing the OH radical reactivity.

