

Investigation of OH radical kinetics with glycine, alanine, serine and threonine in the aqueous phase

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Amino acids are key substances in biological activities and can be emitted into the atmosphere as constituents of primary aerosols. Understanding the radical kinetics of amino acids is necessary to evaluate their atmospheric effects. In the present study, the hydroxyl radical (OH) reaction kinetics of glycine, alanine, serine and threonine were investigated in the aqueous phase. The temperature and pH dependent rate constants were measured by a laser flash photolysis-long path absorption setup using the competition kinetics method. Based on the measurements and speciation calculations, the OH radical reaction rate constants of the fully protonated (H_2A^+) and neutral (HA^\pm) 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 $\text{L mol}^{-1} \text{ s}^{-1}$).

The density functional theory calculation was performed using GAUSSIAN to simulate the energy barriers (E_{Barrier}) of OH radical induced H-atom abstraction. According to the simulated results, amino and carboxyl group increase the E_{Barrier} at the adjacent C-atom and thus reduce the OH radical reactivity. Hydroxide and methyl group decrease the E_{Barrier} at the adjacent C-atom, leading to an increase in the OH radical rate constant.