EGU21-15624
https://doi.org/10.5194/egusphere-egu21-15624
EGU General Assembly 2021

Reaction kinetics of OH radicals with glutaric acid and adipic acid in the aqueous phase

Liang Wen, Thomas Schaefer, and Hartmut Herrmann
Atmospheric Chemistry Department (ACD), Leibniz-Institute for Tropospheric Research (TROPOS), Permoserstrasse 15, 04318 Leipzig, Germany

Dicarboxylic acids (DCAs) are widely distributed in atmospheric aerosols and cloud droplets and are mainly formed by the oxidation of volatile organic compounds (VOCs). For example, glutaric acid and adipic acid are two kinds of the DCAs that can be oxidized by hydroxyl radical (□OH) reactions in the aqueous phase of aerosols and droplets. In the present study, the temperature- and pH-dependent rate constants of the aqueous OH radical reactions of the two DCAs were investigated by a laser flash photolysis-long path absorption setup using the competition kinetics method. Based on speciation calculations, the OH radical reaction rate constants of the fully protonated (H_2A), deprotonated (HA^-) and fully deprotonated (A^{2-}) forms of the two DCAs were determined. The following Arrhenius expressions for the T-dependency of the OH radical reaction of glutaric acid, $k(T, H_2A) = (3.9 \pm 0.1) \times 10^{10} \times \exp[(-1270 \pm 200\ K)/T]$, $k(T, HA^-) = (2.3 \pm 0.1) \times 10^{11} \times \exp[(-1660 \pm 190\ K)/T]$, $k(T, A^{2-}) = (1.4 \pm 0.1) \times 10^{11} \times \exp[(-1400 \pm 170\ K)/T]$ and adipic acid, $k(T, H_2A) = (7.5 \pm 0.2) \times 10^{10} \times \exp[(-1210 \pm 170\ K)/T]$, $k(T, HA^-) = (9.5 \pm 0.3) \times 10^{10} \times \exp[(-1200 \pm 200\ K)/T]$, $k(T, A^{2-}) = (8.7 \pm 0.2) \times 10^{10} \times \exp[(-1100 \pm 170\ K)/T]$ (in unit of L mol^{-1} s^{-1}) were derived.

The energy barriers of the H-atom abstractions were simulated by the Density Functional Theory calculations run with the GAUSSIAN package using the M06-2X method and the basis set m062x/6-311++g(3df,2p). The results showed that the energy barriers were lower at the C_β-atoms and are higher at the C_α-atoms of the two DCAs, clearly suggesting that the H-atom abstractions occurred predominately at the C_β-atoms. In addition, the ionizations can enhance the electrostatic effects of the carboxyl groups, significantly reducing the energy barriers, leading to the order of OH radical reactivity as < < . This study intends to better characterize the losing processes of glutaric acid and adipic acid in atmospheres.