

New method of determining the T-dependent OH radical reaction kinetics in the aqueous phase using the Fenton reaction as a dark OH source

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Abstract

α , β -unsaturated carbonyl compounds are ubiquitous gas-phase constituents and they play an important role in the chemistry of the polluted troposphere. They arise into the atmosphere as primary pollutants from myriad of anthropogenic sources, including incomplete combustion processes and industrial emissions. In addition to direct sources, those molecules are recognized as the first stable products, formed upon atmospheric photooxidation of reactive aromatic compounds. Once α , β -unsaturated carbonyls are present in the gas phase, they can undergo phase transitions from the gas phase into the bulk aqueous phase due to their highly water-soluble characteristics. The oxidation capacity of atmospheric aqueous phase is driven by radical species like NO_3 or OH through a set of recombination reactions with dissolved organics. Additionally, oxidized organics remain in the particle phase upon cloud droplet episode and add to the budget of hygroscopic characteristics of secondary organic aerosols (SOA). Therefore, atmospheric aqueous phase transformations with aqueous radicals is of fundamental importance for better understanding the fate of in-cloud processed SOA.

The new analytical method was implemented to determine the OH radical kinetics of organics using the Fenton reaction ($\text{Fe(II)}/\text{H}_2\text{O}_2$), which can contribute to the production of OH radicals through the catalytic decomposition of H_2O_2 by the means of Fe(II) at acidic and dark conditions in the aqueous phase. The OH-initiated rate constants with the unsaturated dialdehydes, including (1) crotonaldehyde and (2) 1,4-butenedial were elucidated from the bulk aqueous phase reactor using the competition kinetics method. In this novel method, the deuterated isopropanol ($\text{d}8$) serves as radical scavenger, and the deuterated acetone ($\text{d}6$) emerges as the final product through the oxidation reaction with OH radicals, which after derivatization process using PFBHA can be easily detectable with GC-MS. Kinetic results obtained with the newly developed method will be implemented in the CAPRAM model to enhance predictive capabilities.