



Atmospheric Reactions of ozone with a series of cis-3-hexenyl esters: kinetic and mechanistic studies

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Biogenic volatile organic compounds (BVOCs) are believed to play a central role in determining atmospheric composition and the oxidizing capacity of the atmosphere. Many studies have found great discrepancy between measured and simulated OH concentration, total OH reactivity and also the production of ozone. In addition to the uncertainty in the understanding of VOCs emissions, the lack of systematic understanding on the reaction process of identified VOCs is also an important reason for this discrepancy. Thus, it is very important to thoroughly study their reaction process, including atmospheric degradation mechanism and kinetic information, for all the VOCs emitted into the atmosphere.

As an important group of green leaf volatiles (GLVs), C6 hexenyl esters are found to be widely emitted into the atmosphere by plants and vegetation, especially when they suffer mechanical damage. Although reaction with OH may be the dominant degradation pathway for these esters in the atmosphere, reaction with O₃ may also play an important role, especially in polluted areas.

In this presentation, the rate constants for reactions of O₃ with a series of cis-3-hexenyl esters have been measured using absolute method in a flow tube reactor at 298K and atmospheric pressure. Theoretical calculations were also carried out for the title reactions to better understand their kinetics and mechanism using density functional theory (DFT) and transition state theory (TST). Geometry optimizations, energy and the harmonic vibrational frequency calculations were performed for all of the stationary points at the BHandHLYP/6-311+G(d,p) level of theory. The calculated rate constants were in good agreement with the experimental values. The results showed that the reactivity of the studied compounds towards O₃ was obviously dependent on their chemical structure, such as the nature of the substituent, and the relative positions of the double bond and the substituent. The results were also discussed in terms of their atmospheric importance in the degradation of these unsaturated esters by comparing their lifetimes with respect to their reactions with O₃ and other main atmospheric oxidants.

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