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Kinetics of the $C_3H_5 + O_2$ reaction investigated by photoionization using synchrotron radiation

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The kinetics of the ubiquitous allyl radical, C_3H_5 , with molecular oxygen has been studied at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source. The new CRF-PEPICO (Combustion Reactions Followed by Photoelectron Photoion Coincidence Spectroscopy) setup uses a slow flow tube reactor and enables the recording of threshold photoelectron spectra necessary for a background free, isomer selective analysis of the reaction. We compared the rate constants of direct and indirect sources of allyl radicals. Photolysis of allyl iodide at 266 nm and 213 nm was used as a direct source, and H-atom abstraction of propene by Cl atoms, generated from photolysis of oxalyl chloride, as an indirect one. All experiments used Ar as bath gas and were performed at room temperature with an excess of oxygen to maintain pseudo-first order conditions and at various pressures from 0.8 to 3 mbar. Although the allyl radical could be observed and identified, the main reaction product the allyl peroxy was not observed. This can be attributed to the very weakly bound allyl peroxy cation leading to dissociative photoionization. From the concentration-time profiles of the allyl radical second order rate constants between $1.35 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.75 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 3 mbar were determined. While the rates for the direct and indirect generation of allyl radicals agree well with each other, the found rate constants are about a factor 2 higher than reported values in the literature. In part the reason for this may be the use of He as bath gas, resulting a lower collision efficiency causing a different fall-off behavior. Using the photolysis of oxalylchloride to generate allyl radicals an interesting product is observed at $m/z = 68$, which could be identified as 1,3-butadienal by its threshold photoelectron spectrum. A possible formation mechanism involves the reaction between allyl the intermediately generated COCl radical from the 266 nm photolysis of oxalyl chloride.

Summary

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