

248nm photolysis of acetaldehyde: quantum yield of H and HCO and rate constant of the reaction CH₃ + HO₂

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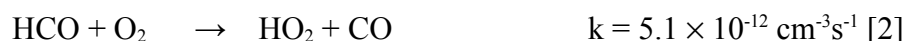
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Acetaldehyde is an important carbonyl compounds present in the atmosphere as it is emitted to the atmosphere from plants, combustion processes etc. Its photodecomposition by sunlight generates free radicals which further influence the photochemistry of the troposphere. Recently, Moortgat et al. [1] investigated the photolysis of acetaldehyde in the wavelength range of 255 to 335 nm and provided quantum yields for the three primary photolysis processes (R1a), (R1b) and (R1c) by measuring stable end products using GC/FID.



Products from (R1a) and (R1c), HCO radicals and H atoms, react with O₂, but with very different rate constants:



Therefore, measuring the time resolved HO₂ kinetics at different [O₂] using laser photolysis / cw-CRDs setup provides a direct measure of the quantum yields for HCO and H atom formation from the acetaldehyde photolysis at 248 nm.

In the same system, the reaction of CH₃ with HO₂ can be studied: this reaction can play, under certain conditions (moderate temperature and high pressure), a key role in combustion processes, as HO₂ and CH₃ radicals are the dominant species in the radical pool. The reaction CH₃+ HO₂ competes with the CH₃ self recombination as the major sink for CH₃. Competition between both reactions is important as the CH₃ self recombination is a chain terminating step whereas the reaction of CH₃+HO₂ can produce new radical species such as OH and CH₃O. The only reports available in the literature concerning this reaction are theoretical calculations [4,5], to our knowledge no experimental determinations of the rate constant has been published. Both HO₂ and CH₃ radicals are formed during the photolysis of acetaldehyde, which allows determining the rate constant for CH₃ + HO₂ experimentally by modelling the time resolved decays of HO₂ radicals under different experimental conditions (photolysis energy, initial CH₃CHO and O₂ concentrations).

References

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