

CH₂OO Criegee Decomposition Kinetics

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Recent interest in Criegee intermediates, produced in the atmosphere following the ozonolysis of unsaturated volatile organic compounds (VOCs),¹ has largely focused on the chemistry of their bimolecular reactions.^{2,3} However, the unimolecular decomposition reactions of stabilised Criegee intermediates are potentially significant as loss mechanisms in the atmosphere, and have been proposed as potential sources of interferences in field measurements of OH radicals.⁴ Production of the Criegee intermediate CH₂OO in the combustion of the biofuel dimethyl ether has also been predicted,⁵ with unimolecular decomposition likely to be important under combustion conditions.

In this work, we report the results of an investigation of the unimolecular decomposition kinetics of CH₂OO, the first Criegee intermediate in the homologous series, generated following the flash photolysis of CH₂I₂ in the presence of excess O₂. Experiments have been performed as a function of temperature and pressure using two complementary techniques.

Direct monitoring of CH₂OO was achieved in UV absorption experiments at temperatures between 450 K and 650 K and pressures in the range 2 – 300 Torr, with measurements in both He and N₂ bath gases. Laser-induced fluorescence (LIF) spectroscopy experiments were also conducted over a range of temperatures (500 – 680 K) and pressures (10 – 95 Torr) to monitor the production of OH radicals following decomposition of CH₂OO. Results indicate that OH is a minor reaction product in the system and unlikely to contribute to potential interferences in measurements of OH radicals in the atmosphere.

Experimental results have been used to constrain Master Equation calculations using the Master Equation Solver for Multi Energy-well Reactions (MESMER)⁶ to model the decomposition reaction and to enable a full description of the decomposition kinetics as a function of temperature and pressure.

References

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