

# Multiplexed Photo-Ionization Mass Spectrometry Investigation of the Acetyl Peroxy + HO<sub>2</sub> Reaction

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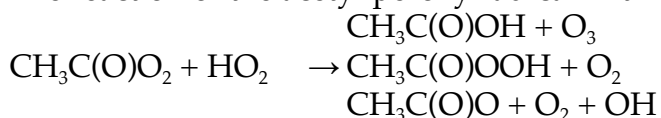
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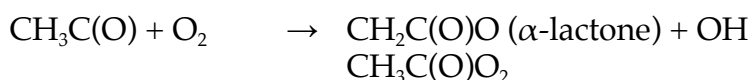
Peroxy radicals are important intermediates in the oxidation of Volatile Organic Compounds (VOCs) in the troposphere, and play a crucial role in air pollution, the formation of photochemical smog and organic aerosols. The acetyl peroxy radical, CH<sub>3</sub>C(O)O<sub>2</sub>, is generated from free radical reactions of carbonyl compounds. Its subsequent chemistry can lead to formation of formic acid, acetic acid, and acetyl nitrate (PAN). A key loss process is the radical-radical reaction with hydroperoxy radical, HO<sub>2</sub>, particularly when nitrogen oxides are low.

The reaction of the acetyl peroxy radical with HO<sub>2</sub> has three product channels:



The third channel was discovered recently, and it may be important in resolving discrepancies between the concentrations of hydroxyl radicals OH observed in the atmosphere and that predicted by models. However, there remains significant disagreement concerning the OH yield among recent laboratory kinetics studies.

Time-resolved photoionization mass spectrometry (PIMS) provides a powerful approach for studying the product branching ratios and reaction rates, by selective time-resolved detection of most of the reactants, intermediates, and primary products. We report our studies of this reaction in a laser-photolysis low-pressure flow cell experiment which utilizes tunable VUV radiation generated at the Advanced Light Source synchrotron at the Lawrence Berkeley Laboratory, coupled to the Sandia multiplexed PIMS apparatus. We are able to determine relative product yields based on measurements of absolute radical concentrations, coupled with kinetic modeling of the time-dependence of the observed species. We have also investigated the acetyl + O<sub>2</sub> reaction



and find significantly different OH yields when compared to the literature.