

Product detection of the CH radical reactions with acetaldehyde and acetone

Fabien Goulay,^{1,*} Adam J. Trevitt,² John D. Savee,³ Jordy Bouwman,⁴ David L. Osborn,³ Craig A. Taatjes,³ Kevin R. Wilson⁴ and Stephen R. Leone^{4,5}

¹ West Virginia University, Morgantown, WV, USA

² University of Wollongong, Wollongong, Australia

³ Sandia National laboratories, Livermore, CA, USA

⁴ University of California at Berkeley, Berkeley, CA, USA

⁵ Lawrence Berkeley National laboratory, Berkeley, CA, USA

* Corresponding author: Fabien.Goulay@mail.wvu.edu

The reaction of methylidyne radical (CH) with carbonyl compounds such as aldehydes, ketones or carboxylic acids is likely to play a central role in the chemical evolution of combustion environments. The CH radical displays very rapid reaction kinetics with formaldehyde¹ and ketene² but the general reaction mechanism with carbonyl compounds is unknown. We have studied the reactions of CH with acetaldehyde (CH₃CHO) and acetone (CH₃CH₂CO) at room temperature using a multiplexed photoionization mass spectrometer coupled to the tunable vacuum ultraviolet synchrotron radiation of the Advanced Light Source. Analysis of photoionization yields versus photon energy for the reaction of CH and CD with acetaldehyde and acetone and CH radical with partially deuterated acetaldehyde (CD₃CHO) elicits fine details about the reaction mechanism.

The reaction with acetaldehyde yields five exit channels.³ The CH₂ elimination channel is found to preferentially form the acetyl radical by removal of the aldehydic hydrogen. The insertion of the CH radical into a C–H bond of the methyl group of acetaldehyde is likely to lead to a C₃H₅O-reaction intermediate that can isomerize by β-hydrogen transfer of the aldehydic hydrogen atom and dissociate to form acrolein + H or ketene + CH₃, which are observed directly. Cyclo-addition of the radical onto the carbonyl group is likely to lead to the formation of the observed products, methylketene (CH₃CH=C=O), methyleneoxirane (c-H₂C=COCH₂), and acrolein (H₂C=CH-CHO). The reaction with acetone produces mainly dimethylketene (CH₃CH₂C=C=O) by elimination of the H-atom initially from the radical and methacrolein (H₂C=CCH₃-CHO) by elimination of an H-atom initially from a methyl-group.

These experimental results suggest that the CH radical can add onto a C=O bond to form cyclic intermediates that further isomerize by ring opening. Elimination of the hydrogen initially from the radical forms substituted ketene molecules while elimination of a hydrogen atom in β-position from the newly inserted carbon atom forms conjugated enal molecules.

References

- (1) Zabarnick, S.; Fleming, J. W.; Lin, M. C. *21st Int. Symp. Comb.* **1986**, 713-719.
- (2) Hancock, G.; Heal, M. R. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 2121-2123.
- (3) Goulay, F.; Trevitt, A. J.; Savee, J. D.; Bouwman, J.; Wilson, K. R.; Osborn, D. L.; Taatjes, C. A.; Leone, S. R. *J. Phys. Chem. A* **2011**, 10.1021/jp2113126.