

Revisiting the Thermal Decomposition of CH₃CHO

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CH₃CHO thermal decomposition has been a subject of numerous studies over the past 80 years with the essential mechanistic features remaining largely unchanged from the early propositions of Rice and Herzfeld [1]. Initiation through C-C bond fission is the only active channel considered in low temperature [2] or high temperature studies [3]. However, this well characterized decomposition has merited renewed scrutiny in the combustion and gas phase chemical physics community for two main reasons.

1. This is an intermediate that appears in copious amounts when combusting new generation oxygenated fuels, as such or in blends, with conventional fuels [4].
2. Recent experimental [5,6] and theoretical [7] studies have suggested new mechanistic thermal decomposition pathways not considered in prior literature studies.

Recent shock-tube experiments from our laboratory [5] were prompted by the observations of an active “roaming” mechanism forming molecular products (CH₄ + CO) in the photodissociation of CH₃CHO [8]. These experiments utilized ultra-sensitive H-ARAS with very dilute [CH₃CHO]₀ and determined yields of H-atom forming channels to be ~ 0.8. With the aid of high-level electronic structure calculations, theoretical kinetics predictions were in quantitative agreement with experiment and indicated that the H-atom yield was only due to C-C bond fission and the non H-atom yield was primarily due to the “roaming” mechanism. However, recent pyrolysis studies on protonated and deuterated acetaldehyde in a micro-tubular reactor by Vasiliou et al. [6] question the validity of the proposed “roaming” mechanism based on observations of vinyl alcohol, ketene, acetylene, and water using sensitive detection techniques. CH₂CHOH is proposed to be a dominant intermediate in this study [6] with subsequent products being produced from unimolecular reactions of CH₃CHO and CH₂CHOH.

In this work we have refined the sub-mechanism for acetaldehyde pyrolysis as part of ongoing modeling efforts on ethanol combustion. The C₂H₄O and C₂H₅O potential energy surfaces have been revisited with theoretical kinetics predictions for relevant channels in acetaldehyde and vinyl alcohol. The present theoretical predictions indicate a minor role for vinyl alcohol in CH₃CHO decomposition in accord with our recent experiments [5] and theory [7]. Modeling indicates that the observations of ketene, acetylene, and water in the recent study of Vasiliou [6] are due to secondary reactions and have no bearing on the initiation steps for CH₃CHO decomposition.

References

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