

# An Experimental and Theoretical Study of the Thermal Decomposition of 1,3-Butadiene

James P. A. Lockhart,<sup>1</sup> C. Franklin Goldsmith,<sup>2</sup> John B. Randazzo,<sup>1</sup> and Robert S. Tranter<sup>1,\*</sup>

<sup>1</sup> Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, 60439, United States

<sup>2</sup> School of Engineering, Brown University, Providence, RI, 02912, United States

\* Corresponding author: tranter@anl.gov

1,3-Butadiene (1,3-C<sub>4</sub>H<sub>6</sub>) is a common intermediate in combustion chemistry and the thermal decomposition of this conjugated diene has been studied extensively using a range of techniques.<sup>1–7</sup> Despite numerous experimental investigations, the exact nature of the initial step involved in the thermal decomposition of 1,3-C<sub>4</sub>H<sub>6</sub> remains poorly understood, with pathways to either radical,<sup>1,2</sup> molecular,<sup>3,4</sup> or isomerization products<sup>5–7</sup> all proposed in the literature. Here we investigate the thermal decomposition of 1,3-C<sub>4</sub>H<sub>6</sub> inside a diaphragmless shock tube (DFST) over a broad range of pressures (29 – 254 Torr) and temperatures (1760 – 2354 K) using laser schlieren (LS) densitometry to elucidate both the kinetics and decomposition mechanism. The region of the potential energy surface pertinent to the thermal decomposition of 1,3-C<sub>4</sub>H<sub>6</sub> has been calculated using high level theory, and confirms the radical and molecular dissociation channels reported elsewhere, as well as isomerization pathways to either 1,2-butadiene (1,2-C<sub>4</sub>H<sub>6</sub>) or 1-butyne (1-C<sub>4</sub>H<sub>6</sub>). Both 1,2-C<sub>4</sub>H<sub>6</sub> and 1-C<sub>4</sub>H<sub>6</sub> can in turn dissociate directly to CH<sub>3</sub> + C<sub>3</sub>H<sub>3</sub>. Rice-Ramsperger-Kassel-Marcus/Master Equation theory has been used to compute phenomenological rate coefficients for the various product paths associated with this complex multi-well surface and identified a formally direct dissociation path along which 1,3-C<sub>4</sub>H<sub>6</sub> can fragment directly to CH<sub>3</sub> + C<sub>3</sub>H<sub>3</sub> products. To the best of our knowledge this is the first investigation of 1,3-C<sub>4</sub>H<sub>6</sub> decomposition to consider a formally direct dissociation pathway. Successful simulation of the experimental LS density gradient profiles not only necessitates a model that includes this formally direct dissociation path, but reveals this channel as the dominant loss process for 1,3-C<sub>4</sub>H<sub>6</sub> under the conditions of this study. Complementary LS experimental studies of 1,2-C<sub>4</sub>H<sub>6</sub>, 1-C<sub>4</sub>H<sub>6</sub> and 2-C<sub>4</sub>H<sub>6</sub> have been carried out and an internally consistent model developed that can successfully simulate the experimental density gradient profiles of all four isomers over a broad range of conditions.

## References

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