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SHOCK TUBE/LASER ABSORPTION STUDIES OF THE DECOMPOSITION OF FUEL SURROGATES

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ABSTRACT

The high-temperature decomposition of two rocket fuel (kerosene) surrogate components, n-dodecane and methylcyclohexane (MCH), have been studied using laser absorption in both high- and low-pressure shock tubes. Species time-histories of both the parent fuel and the primary decomposition product, ethylene, were recorded during the high-temperature pyrolysis of these fuels using IR laser absorption. Fuel mole fraction was monitored using absorption of an IR HeNe laser at 3.39 μm and ethylene mole fraction was monitored using absorption of the P14 line of a CO_2 gas laser near 10.53 μm . Measurements provide overall fuel-decomposition rate constants for both fuels and these measurements are further related to elementary reaction rate constants for n-dodecane decomposition. The species time-history data provide unique kinetic targets for the testing and validation of RP-fuel surrogate mechanisms. In particular, fuel decomposition rate and ethylene yield data were used to test fuel decomposition reaction rates and pathway branching ratios found in current reaction mechanisms.

INTRODUCTION

To maintain structural integrity, rocket engines are cooled by circulating rocket fuel in cooling channels along the combustion chamber walls. Higher engine thrust can be achieved if the rocket engine walls can be maintained at higher temperatures. These higher wall temperatures cause the rocket fuel to experience higher temperatures in the cooling channels. The behavior of rocket fuel at these higher temperatures is not well-known, and high-fidelity models of rocket fuel chemistry at these higher temperatures are needed.

The rocket fuel chemistry in the cooling channels can be divided into fuel-wall processes and fuel decomposition processes. At the higher temperatures now being considered for higher-thrust engines, the fuel decomposition processes are accelerated and result in a significant change in the composition of the fuel being carried in the cooling channels. The high-temperature and high-pressure (i.e. super-critical) fuel decomposition chemistry now possible in these cooling channels is similar to that found in high-temperature gas-phase systems.^{1,2,3,4,5} Because of this, techniques, facilities and models used to study gas-phase combustion processes, in particular shock tubes, laser absorption and detailed reaction mechanisms, can be directly applied to the study of rocket fuel surrogate pyrolysis.⁶

Distillate rocket fuels, such as RP-1 and RP-2, are comprised of hundreds of individual components. A comprehensive detailed reaction mechanism describing the chemistry of all these components is neither possible (because of computational limitations) nor necessary (because of the chemical similarity of many of the components) at present. What can and should be accomplished, however, is the development of a surrogate fuel and a detailed reaction mechanism for this surrogate fuel that can closely simulate the behavior of RP-fuels during high-temperature pyrolysis.

Previous studies of kerosene-based fuels, such as JP-8 and Jet A, have approached the problem of creating a surrogate fuel mixture by using archetypal examples of the major general classes of chemical components found in the fuel.^{7,8} The dominance of n-alkane and cycloalkane species in kerosene-based fuels suggests that a simple two-component surrogate created from a combination of n-dodecane ($C_{12}H_{26}$) and methylcyclohexane (MCH) (C_7H_{14}) may be able to duplicate many of the chemical properties of RP-series fuels. Thus, this two-component surrogate fuel should in fact better predict the decomposition product distribution of RP-fuels than a single-component surrogate fuel such as neat n-dodecane or MCH.

Two main characteristics are relevant in fuel decomposition processes: the overall rate of decomposition of the dominant fuel components, and the distribution of decomposition products. Representative measurements of the overall fuel-decomposition rate constants for kerosene and large n-alkane are shown in Figure 1; significant variation is seen amongst these studies. However, while there is a multiplicity of lower-temperature studies of n-alkanes, only a limited number of measurements of the decomposition rate constants for RP-fuels exist.⁹ As well, though extensive studies exist to describe species time-histories during n-dodecane oxidation,¹⁰ little, if any, work exists to describe the species time-histories during the pyrolysis of n-dodecane, MCH or mixtures of these two components. Species time-history measurements of the dominant n-alkane decomposition product ethylene are particularly needed because of the important role this species can play in soot production.^{4,11,12}

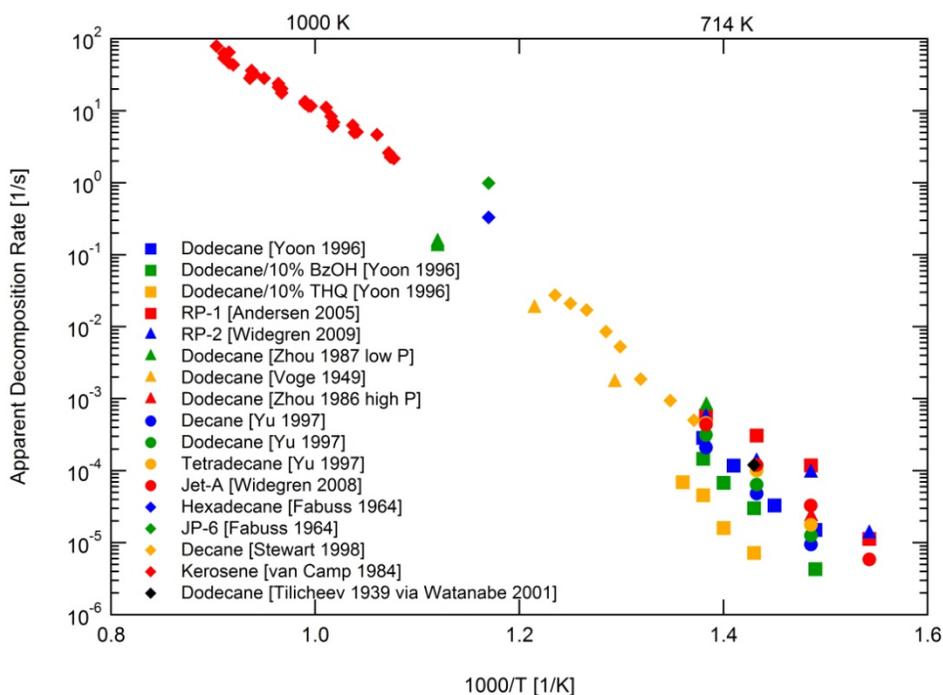


Figure 1. Overall fuel-decomposition rate constants for kerosene and large n-alkanes: Yoon 1996,¹³ Andersen 2005,⁹ Widegren 2009,¹⁴ Zhou 1987,¹⁵ Voge 1949,¹⁶ Zhou 1986,¹⁷ Yu 1997,¹⁸ Widegren 2008,¹⁹ Fabuss 1964,²⁰ Stewart 1998,¹ Van Camp 1984,²¹ Watanabe 2001.²²

These two main characteristics are only two of the observables of a more comprehensive detailed reaction mechanism that describes fuel decomposition. Recently, several detailed reaction mechanisms have been developed to model n-dodecane and MCH oxidation.^{23,24,25,26,27} These mechanisms are comprised of hundreds of species and hundreds to thousands of reactions, the large majority of which have only estimated reaction rate constants. Stripped of their oxygenate sub-mechanisms, any of these mechanisms can be used as the basis for the development of an RP-fuel surrogate mechanism. These detailed reaction mechanisms can be used to predict not only overall fuel-decomposition rate constants and product distributions, but also transient intermediate species time-histories. However, the accuracy of these reaction mechanisms must be validated by comparison with measured species time-histories. Modification of individual reaction rate constants or the addition of new reaction pathways, properly guided by theory, can then be used to bring modeled and measured species time-histories into agreement and refine the performance of the detailed reaction mechanism. Experiments using shock tube/laser absorption techniques can provide the needed validation for these detailed reaction mechanisms.

Here, we present measurements of species concentration time-histories behind reflected shock waves in both the n-dodecane and MCH pyrolysis systems. N-dodecane and MCH were measured using laser absorption at $3.39 \mu\text{m}$, and C_2H_4 , the dominant alkane fuel-decomposition product, was measured using laser absorption at $10.53 \mu\text{m}$. These measurements are then used to determine overall fuel-decomposition rate constants and elementary reaction rate constants for the reactions of fuel \rightarrow products.

EXPERIMENTAL SETUP

Measurements were performed behind reflected shock waves in two helium-driven shock tubes: a 15.3 cm diameter low-pressure shock tube, and a 5 cm diameter high-pressure shock tube. Reflected shock temperatures and pressures were calculated based on incident shock speeds using the standard frozen-chemistry shock equations. Test gases were mixed in stainless-steel heated tanks ($60\text{-}90^\circ\text{C}$) and

composed of mixtures of 99.5% n-dodecane or MCH (Sigma-Aldrich) and 99.999% argon. Fuel concentrations, determined manometrically in the mixing tank, were confirmed in the shock tube (*in situ*) using the same IR laser absorption setup used to monitor the fuel time-histories.

Measurements of fuel and ethylene concentration were performed using IR laser absorption. Fuel (n-dodecane or MCH) was detected using mid-IR absorption of He-Ne laser radiation at 3.39 μm following the scheme of Klingbeil et al.²⁸ Ethylene was detected using absorption of the P14 emission line of a CO₂ gas laser at 10.53 μm .²⁹ The experimental setup for this laser is shown in Figure 2.

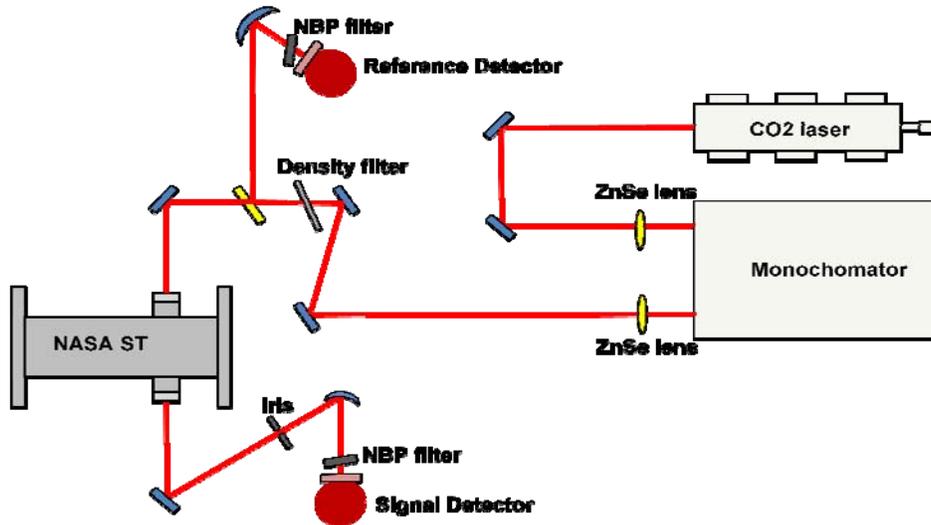


Figure 2. Experimental setup for detection of ethylene at 10.53 μm .

Radiation from an Access Laser Systems model LASY-5 CO₂ gas laser was passed through a monochromator (to ensure single-wavelength operation) and separated into a reference beam (I_0) and transmitted beam (I) that was passed through sapphire windows located 2 cm from the endwall of the shock tube. Narrow-bandpass filters were used to reduce the effect of emission. Each beam was detected using LN₂-cooled InSb detectors. Further details concerning this detection scheme can be found in Pilla et al.²⁹

RESULTS AND DISCUSSION

OVERALL FUEL-DECOMPOSITION RATE CONSTANT MEASUREMENTS

Overall fuel-decomposition rate constants, k_{fuel} , were measured for n-dodecane and MCH for temperatures from 1098 to 1430 K and pressures of 2 to 8 atm and 15 to 45 atm. k_{fuel} was determined from the change in absorption at 3.39 μm at early times assuming:

$$d[\text{fuel}]/dt = -k_{\text{fuel}} [\text{fuel}]$$

Fuel concentration [fuel] was determined from the measured absorption $(I_0 - I)/I_0$:

$$-\ln(I/I_0) = [\text{fuel}] \sigma_{\text{fuel}} L = \text{measured absorbance}$$

where σ_{fuel} is the 3.39 μm absorption cross-section for the fuel and L is the experimental path length (i.e. shock tube diameter).

Figure 3 shows representative low-pressure n-dodecane fuel-decomposition data. At long times, absorbance from the final product species is evident and has an absorbance level of approximately 20% of the initial fuel absorbance (i.e. $\sigma_{\text{fuel}} \sim 5 \sigma_{\text{product}}$). the measured overall fuel-decomposition rate constant can be corrected based on this ratio. By assuming only two absorbers (i.e. fuel and product) are present in the system and that the product is formed directly from the decomposing fuel:

$$d[\text{product}]/dt = + k_{\text{fuel}} [\text{fuel}],$$

the resulting corrected overall fuel-decomposition rate constant is given by:

$$k_{\text{fuel,corr}} = k_{\text{fuel}} (\sigma_{\text{fuel}}) / (\sigma_{\text{fuel}} - \sigma_{\text{product}}).$$

This assumption will produce corrected overall fuel-decomposition rate constants, $k_{\text{fuel,corr}}$ that are approximately one-quarter greater than those without the correction. Measured k_{fuel} values are shown in Figure 4. No strong variation of k_{fuel} with pressure is seen over the range from 2 to 45 atm. Also shown are data from an earlier study from our laboratory (P~7 atm) using an aerosol shock tube methodology.³⁰

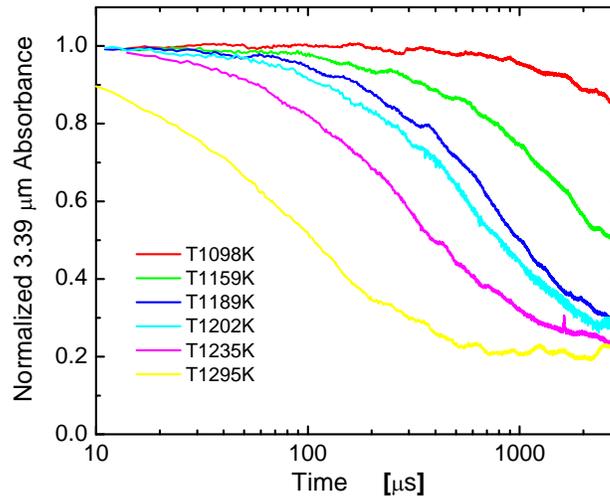


Figure 3. Normalized absorbance measurements during n-dodecane pyrolysis. Initial n-dodecane concentrations vary from 380 to 430 ppm, and initial reflected shock pressure vary from 2.3 to 2.7 atm. Absorbance normalized to unity at t=0.

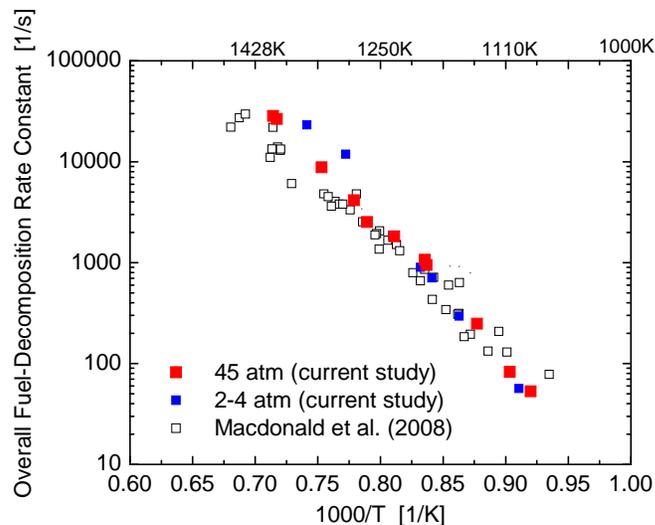


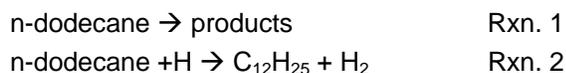
Figure 4. Overall fuel-decomposition rate constant, k_{fuel} , measurements for n-dodecane.

DETERMINATION OF THE REACTION RATE CONSTANT FOR N-DODECANE \rightarrow PRODUCTS

We have applied a more thorough analysis of fuel-decomposition data, based on individual species absorption cross-sections and time-histories of the fuel and the intermediate and final products, to a related n-alkane, n-heptane. That analysis confirmed the general validity of the simple correction model developed in the previous section.³¹ This is because absorption is dominated either by fuel (n-heptane) at early times or by the final alkene products such as ethylene and propene at long times. Intermediate product species such as C_2H_5 and C_3H_7 exist at very low concentration and do not contribute significantly to the absorption at $3.39 \mu\text{m}$. Thus the change in the $3.39 \mu\text{m}$ absorption, corrected for the long-time plateau absorption of the final products, represents the change in n-heptane concentration. The change in absorption is most sensitive to the rate constant of the reaction n-heptane \rightarrow products, and thus the $3.39 \mu\text{m}$ absorption data during pyrolysis can be related to the elementary reaction rate constant, k , of the reaction n-heptane \rightarrow products.

A similar analysis can be performed for n-dodecane pyrolysis. (In the following discussion, constant-volume simulations were performed using the CHEMKIN suite and the n-dodecane reaction mechanism of Sirjean et al. (2009)/JetSurF.²³)

Concentration time-histories of the major species occurring during n-dodecane pyrolysis are shown in Figure 5. The dominant stable decomposition products predicted by the JetSurF reaction mechanism are the alkenes: ethylene, propene and 1-butene. A rate of production (ROP) plot, Figure 6, shows that n-dodecane is removed by the reactions:



with the removal by Rxn. 2 significantly faster than Rxn. 1 at the early times.

However, the rate of removal of n-dodecane is controlled only by the rate constant of Rxn. 1. This is evident from the sensitivity plot shown in Figure 7. The normalized sensitivity coefficients, $S_i = d[\text{n-dodecane}]/dk_i$ ($k_i/[\text{n-dodecane}]$), show that the n-dodecane decomposition reaction rate constant (k_1) has the largest influence on the rate of change of n-dodecane concentration. Though n-dodecane is removed by Rxn. 2, Rxn. 2 reaction is so fast that varying its rate constant (within reasonably possible values) does not have a strong effect on the change in n-dodecane concentration.

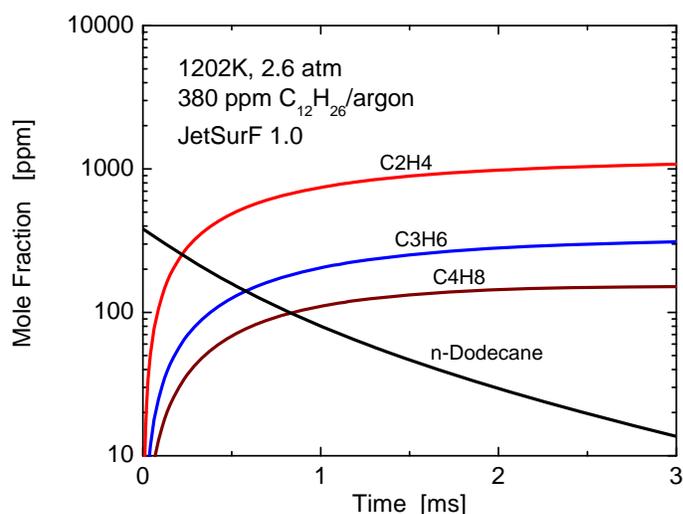


Figure 5. Simulated species concentration time-histories during n-dodecane pyrolysis. Initial reflected shock conditions: 380 ppm n-dodecane/argon, 1202 K, 2.66 atm. Only major species are shown.

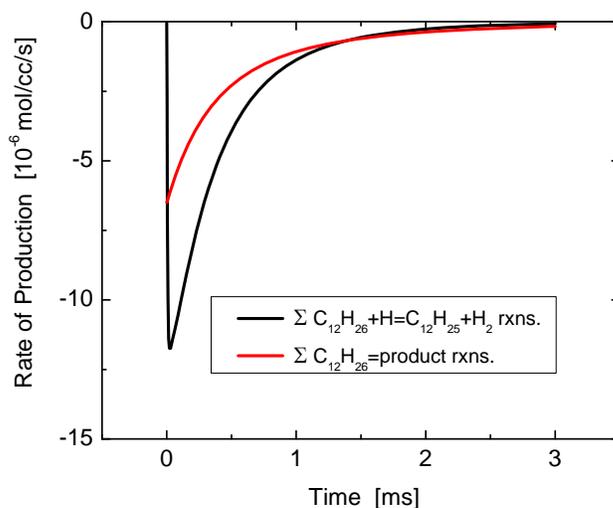


Figure 6. Rate of production plot for 1202 K case shown in Figure 3. Initial conditions: 380 ppm n-dodecane/argon, 1202 K, 2.66 atm. Only the two major reaction types are shown.

The change in the measured $3.39 \mu\text{m}$ absorption, corrected for the long-time plateau absorption of the final products, represents the change in n-dodecane concentration. Because of this strong sensitivity to Rxn. 1, we are able to determine a best-fit value of the rate constant of Rxn. 1 by varying that rate constant in the reaction mechanism until the simulation agrees with the measured absorbance signal that at early times is dominated by the n-dodecane concentration. Figure 8 shows the results of a preliminary determination of a the best-fit simulation for an n-dodecane pyrolysis experiment at 1202 K.

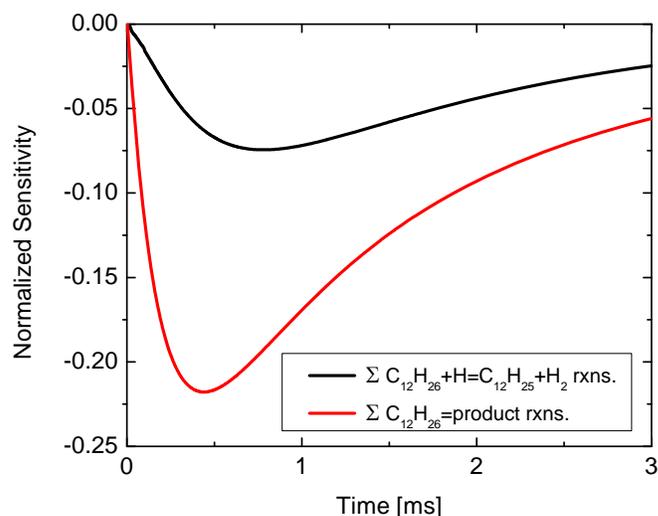


Figure 7. Sensitivity plot for 1202 K case shown in Figure 3. Initial conditions: 380 ppm n-dodecane/argon, 1202 K, 2.66 atm. Only the two major reaction types are shown.

k_1 from the preliminary determination is plotted on Figure 9. The best-fit value of k_1 at 1202 K is approximately 80% of the value used in the JetSurF reaction mechanism and agrees with the JetSurF value within the uncertainty ($\pm 30\%$) of both determinations. The decomposition rate constant, k_1 , for n-dodecane is similar to the values for a smaller n-alkane, n-heptane. Further analysis of the complete set of n-dodecane pyrolysis data is ongoing, and the rate constants derived from that analysis will be used in establishing a refined n-dodecane pyrolysis reaction mechanism.

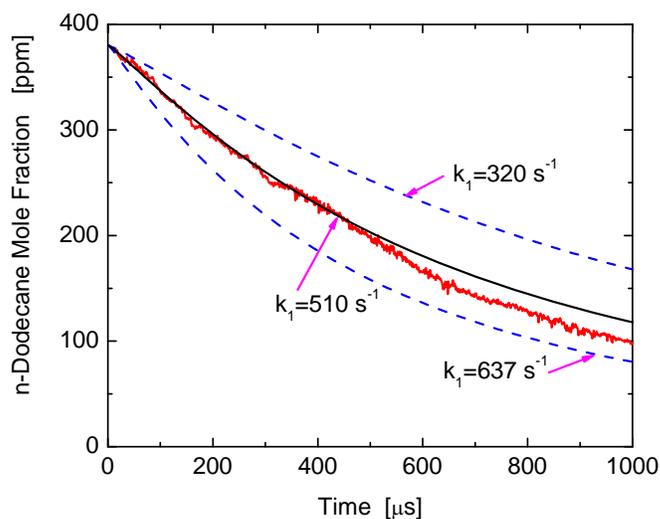


Figure 8. N-dodecane time-history during pyrolysis: JetSurF model and IR absorption data. Initial reflected shock conditions: 1202 K, 2.66 atm, 380 ppm n-dodecane/argon. Best-fit value of $k_1 = 510 \text{ s}^{-1}$.

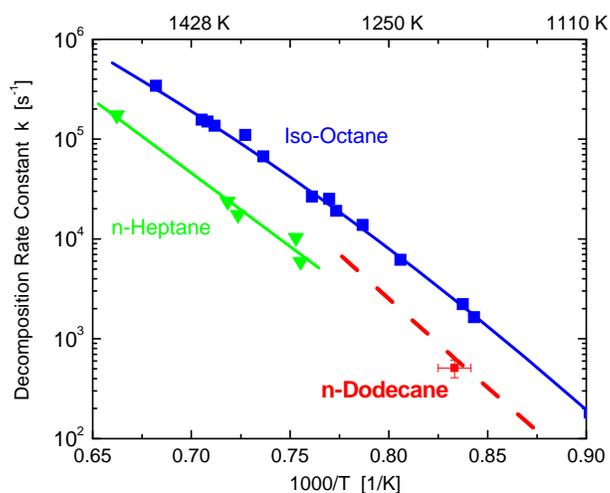


Figure 9. Decomposition reaction (Rxn. 1) rate constant for selected alkanes. Data for n-heptane and iso-octane are taken from Davidson et al.³² Solid lines, best fit to data; dashed red line is from Sirjean et al. (2009).²³

OVERALL FUEL-DECOMPOSITION RATE CONSTANT FOR METHYLCYCLOHEXANE

Figure 10 presents 3.39 μm laser absorption measurements during MCH pyrolysis. In these experiments the final product absorption is relatively smaller than in the n-dodecane experiments and the absorption cross-sections tend towards a ratio of $\sigma_{\text{MCH}} / \sigma_{\text{product}} = 1500/200 \sim 7.5$. This results in corrected overall fuel-decomposition rate constants, $k_{\text{MCH,corr}}$, that are only 15% larger than the uncorrected values, k_{MCH} .

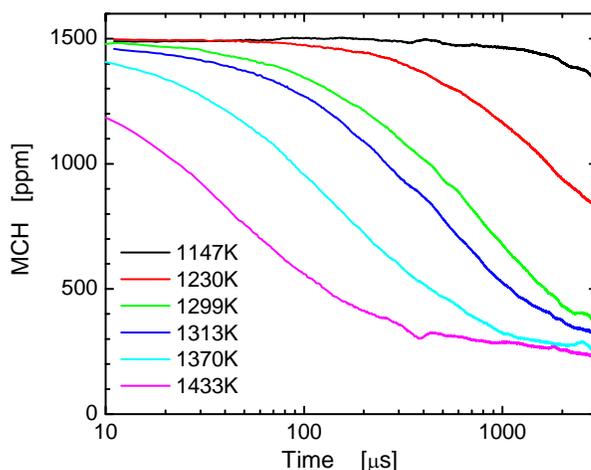


Figure 10. Measured MCH concentration time-histories during pyrolysis. Initial reflected shock conditions: 1500 ppm MCH/argon, 2.1-2.5 atm.

Overall fuel-decomposition rate constants for MCH, k_{MCH} , are shown in Figure 11, along with measurements for n-dodecane from the current study. The overall fuel-decomposition rate constant for MCH is approximate one-sixth of the rate constants for n-dodecane. The activation energies for both

fuels are approximately the same with $E_A = 70.2$ kcal/mol indicating that reactions that break bonds with similar energies (C-C bonds in the fuel) control the rates of decomposition for these two fuels.

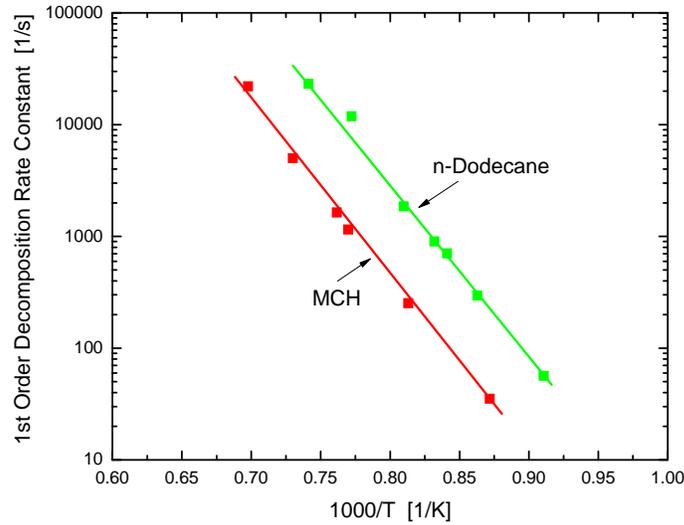


Figure 11. Overall fuel-decomposition rate constant measurements for MCH and n-dodecane: 2-3 atm.

ETHYLENE YIELDS BASED ON TIME-HISTORY ABSORPTION MEASUREMENTS

Ethylene concentration time-histories measured using laser absorption at $10.53 \mu\text{m}$ during n-dodecane and MCH pyrolysis are shown in Figures 12 and 13. Rapid formation to a plateau level is seen for both fuels at all temperatures studied.

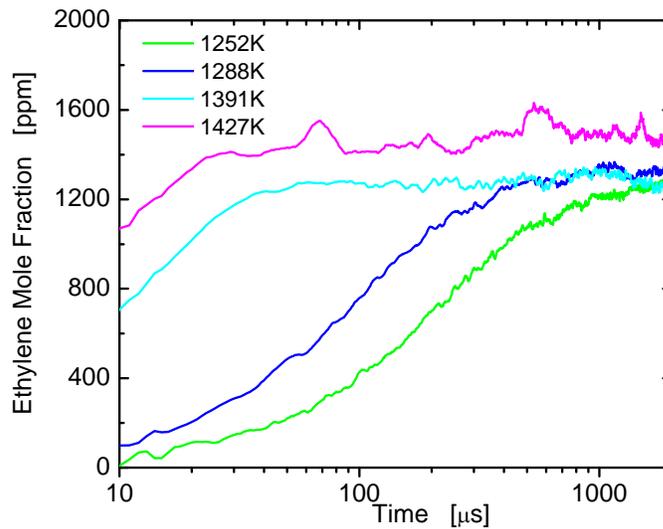


Figure 12. Ethylene time-histories during n-dodecane pyrolysis. Initial reflected shock conditions: 430-460 ppm n-dodecane/argon, 2.1-2.5 atm.

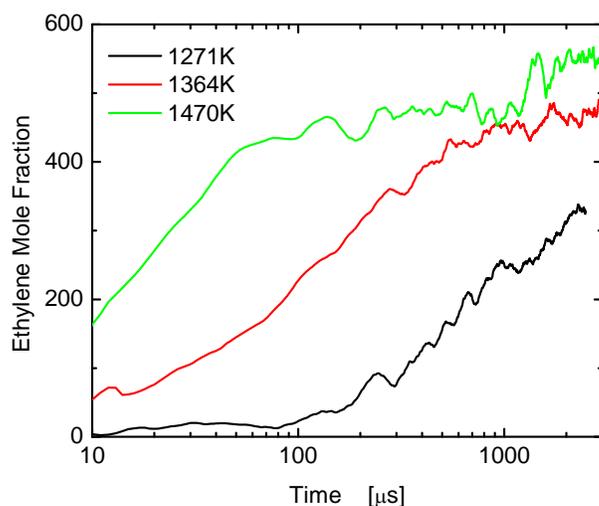


Figure 13. Ethylene time-histories during MCH pyrolysis. Initial reflected shock conditions: 300 ppm MCH/argon, 2.3-2.5 atm.

Representative ethylene time-history data for each fuel are compared to simulations using several current reaction mechanism in Figures 14 and 15 and summary plots of plateau yields of ethylene are shown in Figures 16 and 17. Measured carbon conversion to ethylene for n-dodecane is ~50% ($3 \text{ C}_2\text{H}_4$ per $\text{C}_{12}\text{H}_{26}$) and for MCH is ~43% ($1.5 \text{ C}_2\text{H}_4$ per C_7H_{14}). An important consequence of these carbon conversion values is that the remaining percentage of carbon will take the form of higher alkenes and alkynes (propene, butenes and acetylene) and small alkanes (methane and ethane). Work is currently in progress to measure several of these species in an attempt to understand the final carbon balance and product distribution.

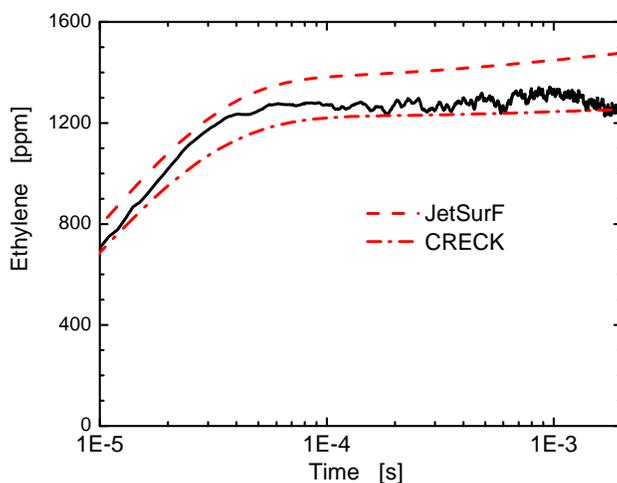


Figure 14. Ethylene concentration time-history during n-dodecane pyrolysis: model and experiment. Initial reflected shock conditions: 1391K, 2.5 atm, 430ppm n-dodecane/argon. Model simulations: JetSurF,²³ CRECK.²⁴

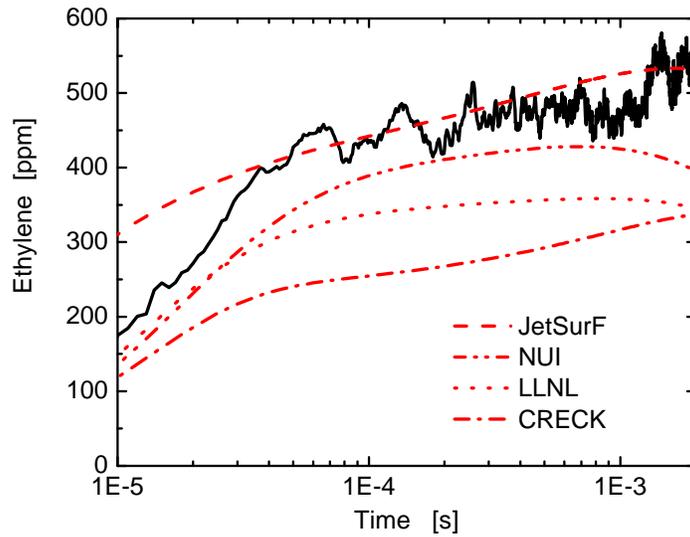


Figure 15. Ethylene concentration time-history during MCH pyrolysis: model and experiment. Initial reflected shock conditions: 1470K, 2.36 atm, 300ppm MCH/argon. Model simulations: JetSurF,²⁵ CRECK,²⁴ NUI,²⁶ LLNL.²⁷

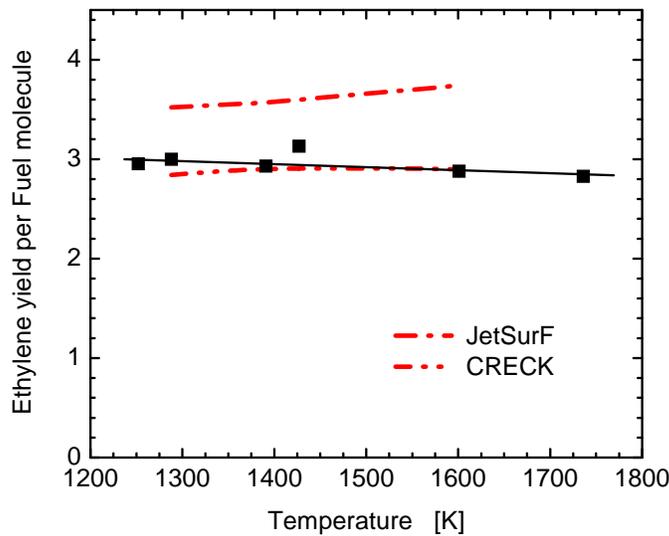


Figure 16. Ethylene yield plot during n-dodecane pyrolysis: model and experiment. Initial reflected shock conditions: 2.1-2.5 atm, 430-460 ppm n-dodecane/argon.

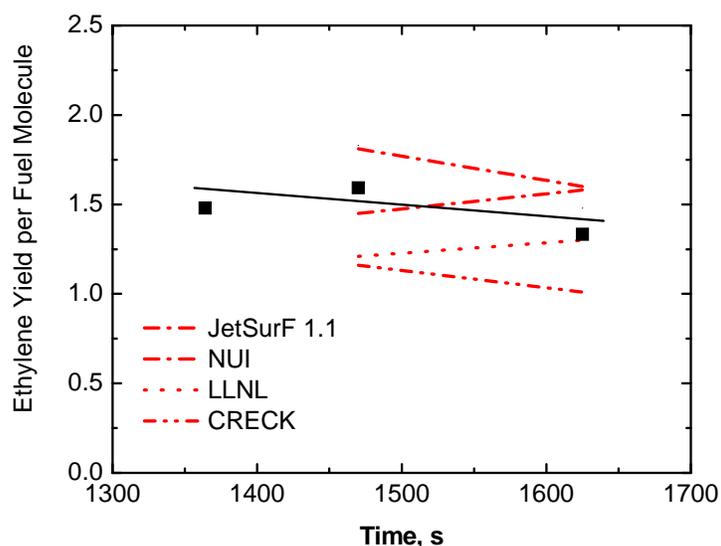
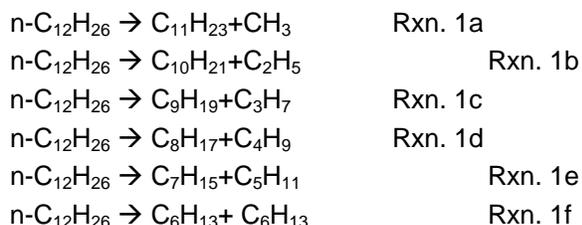


Figure 17. Ethylene yield plot during MCH pyrolysis: model and experiment. Initial reflected shock conditions: 2.3-2.5 atm, 300 ppm MCH/argon.

Ethylene yield data can be used to place constraints on the branching ratios for different decomposition pathways. In the case of n-dodecane,²³ the overall decomposition reaction rate constant k_1 is the sum of the rate constants for the six individual channels:



The intermediate products of these reactions decompose to smaller stable olefins, including ethylene, propene and butene, in various proportions. The actual branching ratios and reaction rate constants of these individual channels and the subsequent reactions that lead from these intermediates to stable final products, are still largely a matter of conjecture. Figures 14-17 indicate the range of variability of the predictions of current mechanisms. We are currently investigating the relationship of the ethylene yields to the n-dodecane rate constants of reactions 1a-1f, and similar decomposition reaction pathways for MCH.

CONCLUSION

Species concentration time-histories for RP-fuel surrogates (n-dodecane and MCH) and the dominant stable alkene product (ethylene) were measured using IR laser absorption behind reflected shocks. Using the fuel time-history measurements, overall fuel-decomposition rate constants were measured and a preliminary determination of the reaction rate constant for n-dodecane \rightarrow products was made. Good agreement with previous overall fuel-decomposition rate constant measurements in our laboratory using an aerosol shock tube was found. The ethylene time-history measurements in both the n-dodecane and MCH pyrolysis systems provide yield data that can be used to place strong constraints on the decomposition reaction product-branching ratios. That work is currently in progress.

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