

Shock Tube Measurement of Alkane Decomposition Using Laser Absorption of CH₃

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Overview

Decomposition rates for alkanes are important initiation steps in the detailed reaction mechanisms describing alkane oxidation and in describing global combustion phenomena such as ignition times. With the development of a CH₃ 216.6 nm laser absorption diagnostic, detailed measurements of five of these reactions have been made in the falloff regime (1300-2000 K and 0.2-8 atm):

- $\text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{CH}_3$
- $\text{C}_3\text{H}_8 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$
- $\text{i-C}_4\text{H}_{10} \rightarrow \text{CH}_3 + \text{i-C}_3\text{H}_7$
- $\text{n-C}_4\text{H}_{10} \rightarrow \text{CH}_3 + \text{C}_3\text{H}_7$
- $\text{n-C}_4\text{H}_{10} \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$

The measurements were made behind incident and reflected shock waves in our high purity kinetics shock tube. The laser absorption diagnostic method provided ppm CH₃ sensitivity while the experiments were of sufficient concentration (100-400 ppm) to be insensitive to impurities and dilute enough to maintain excellent sensitivity to the rate coefficients of interest. Additionally, we only focused on the early time behavior of the CH₃ profiles to maintain isolation of the decomposition reactions and to avoid interfering absorption from other product species that are formed at longer times. Fig. 1 shows an example data trace and sensitivity for ethane; Fig. 2 shows the resulting unimolecular rate coefficients plotted in Arrhenius form.

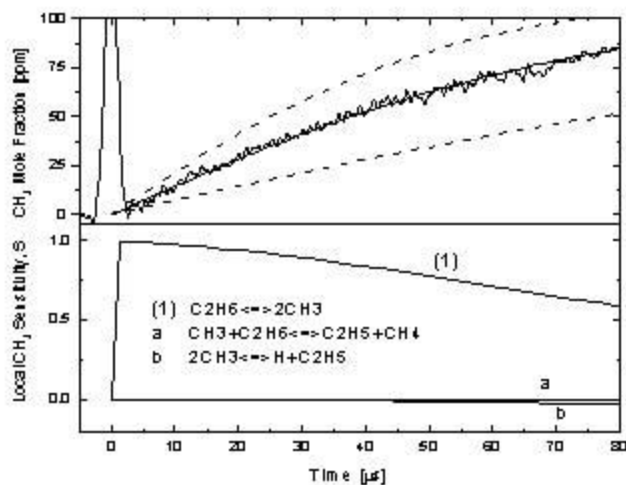


Figure 1: Example ethane data, modeling, and sensitivity. Reflected shock conditions: 1589 K, 1.664 atm, 202 ppm C₂H₆. $S = (dX_{CH_3} / dk_i) (k_i / X_{CH_3,local})$, where k_i is the rate constant for reaction i and $X_{CH_3,local}$ is the local CH₃ mole fraction.

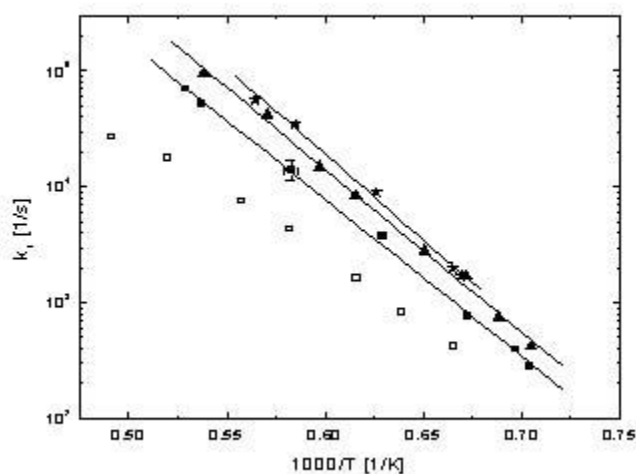


Figure 2: Arrhenius plot for $C_2H_6 = CH_3 + CH_3$. Filled squares, 1.6 atm data; filled triangles, 4.2 atm data; filled stars, 7.5 atm data; open squares, 0.13-0.22 atm data; solid lines, fits to 1.6, 4.2, and 7.5 atm data.

References

1. M. A. Oehlschlaeger, D. F. Davidson, and R. K. Hanson "High Temperature Ethane and Propane Decomposition," 30th Symp. (International) on Combustion, 2004.
2. M. A. Oehlschlaeger, D. F. Davidson, and R. K. Hanson "High Temperature Thermal Decomposition of iso-Butane and n-Butane behind Shock Waves," The Journal of Physical Chemistry A, 108, 4247-4253 (2004).
3. M.A. Oehlschlaeger, D.F. Davidson, and R.K. Hanson: "Shock Tube Measurements of Ethane, Propane, and Butane Decomposition Using Laser Absorption of CH₃," Western States Combustion Institute Meeting, October 20-21, 2003.