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):

- C2H6 → CH3 + CH3
- C3H8 → CH3 + C2H5
- i-C4H10 → CH3 + i-C3H7
- n-C4H10 → CH3 + C3H7
- n-C4H10 → C2H5 + C2H5

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 and example data trace and sensitivity for ethane; Fig. 2 shows the resulting unimolecular rate coefficients plotted in Arrhenius form.

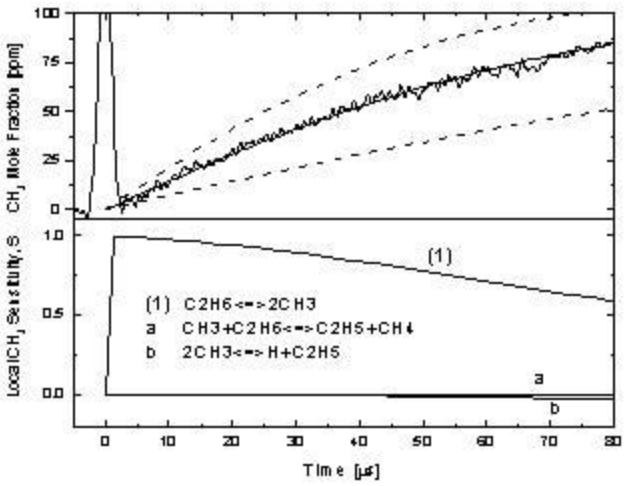

Figure 1: Example ethane data, modeling, and sensitivity. Reflected shock conditions: 1589 K, 1.664 atm, 202 ppm C2H6. S = (dXCH3 / dki) (ki / XCH3,local), where ki is the rate constant for reaction i and XCH3,local, is the local CH3 mole fraction.

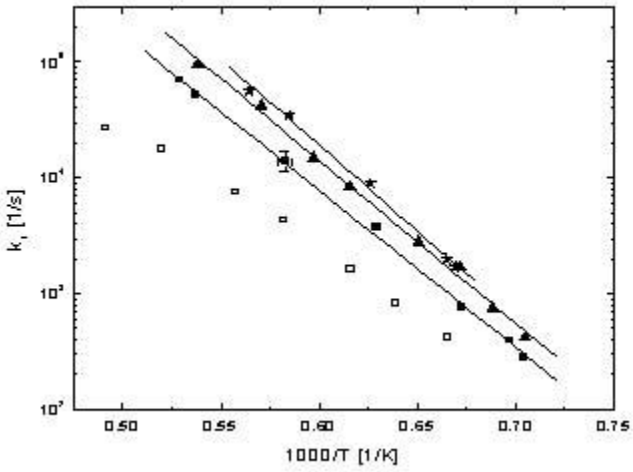

Figure 2: Arrhenius plot for C2H6 = CH3 + CH3. Filled squares, 1.6 atm data; filled triangles, 4.2 atm data; filled stars, 7.5 atm data; open squares, 0.13-0.22 atm data; solid lines, fits to 1.6, 4.2, and 7.5 atm data.

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.