Available online at www.sciencedirect.com

SciVerse ScienceDirect

Proceedings of the Combustion Institute 34 (2013) 607–615

Proceedings of the Combustion Institute

www.elsevier.com/locate/proci

Multi-species time-history measurements during high-temperature acetone and 2-butanone pyrolysis

King-Yiu Lam [a,*], Wei Ren [a], Sung Hyun Pyun [a], Aamir Farooq [b], David F. Davidson [a], Ronald K. Hanson [a]

[a] Department of Mechanical Engineering, Stanford University, Stanford, CA 94305-3032, USA
[b] Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

Abstract

High-temperature acetone and 2-butanone pyrolysis studies were conducted behind reflected shock waves using five species time-history measurements (ketone, CO, CH_3, CH_4 and C_2H_4). Experimental conditions covered temperatures of 1100–1600 K at 1.6 atm, for mixtures of 0.25–1.5% ketone in argon. During acetone pyrolysis, the CO concentration time-history was found to be strongly sensitive to the acetone dissociation rate constant k_1 ($CH_3COCH_3 \rightarrow CH_3 + CH_3CO$), and this could be directly determined from the CO time-histories, yielding $k_1(1.6\text{ atm}) = 2.46 \times 10^{14}\exp(-69.3\text{ [kcal/mol]/RT})\text{ s}^{-1}$ with an uncertainty of ±25%. This rate constant is in good agreement with previous shock tube studies from Sato and Hidaka (2000) [3] and Saxena et al. (2009) [4] (within 30%) at temperatures above 1450 K, but is at least three times faster than the evaluation from Sato and Hidaka at temperatures below 1250 K. Using this revised k_1 value with the recent mechanism of Pichon et al. (2009) [5], the simulated profiles during acetone pyrolysis show excellent agreement with all five species time-history measurements. Similarly, the overall 2-butanone decomposition rate constant k_{tot} was inferred from measured 2-butanone time-histories, yielding $k_{tot}(1.5\text{ atm}) = 6.08 \times 10^{13}\exp(-63.1\text{ [kcal/mol]/RT})\text{ s}^{-1}$ with an uncertainty of ±35%. This rate constant is approximately 30% faster than that proposed by Serinyel et al. (2010) [11] at 1119 K, and approximately 100% faster at 1412 K. Using the measured 2-butanone and CO time-histories and an O-atom balance analysis, a missing removal pathway for methyl ketene was identified. The rate constant for the decomposition of methyl ketene was assumed to be the same as the value for the ketene decomposition reaction. Using the revised k_{tot} value and adding the methyl ketene decomposition reaction to the Serinyel et al. mechanism, the simulated profiles during 2-butanone pyrolysis show good agreement with the measurements for all five species.

Keywords: Shock tube; Acetone; 2-Butanone; Laser absorption

1. Introduction

Ketones are important to a variety of modern chemical processes. As common pollutants, they were of early public health concern because of their toxicities and of environmental concern because of their role in atmospheric chemistry. Interest is now growing in their role in combustion processes. They are widely used as tracers in planar laser-induced fluorescence (LIF) imaging of combustion processes due to their physical similarity to gasoline surrogate components. They are also formed as intermediate products during oxidation

---

* Corresponding author. Address: Department of Mechanical Engineering, Stanford University, 452 Escondido Mall, Building 520, Room 520 I, Stanford, CA 94305-3032, USA. Fax: +1 650 723 1748.
E-mail address: klam1@stanford.edu (K.-Y. Lam).

1540-7489/$ - see front matter
http://dx.doi.org/10.1016/j.proci.2012.06.009

of large oxygenated fuels, such as alcohols and methyl esters. And in contrast to other oxygenated fuels, very little experimental data are available for the larger ketones such as 2-butanone.

Unlike larger ketones, the pyrolysis of acetone has been studied by many researchers, particularly at temperatures below 1000 K. At temperatures above 1000 K, five recent studies have been performed. Capelin et al. [1] examined acetone pyrolysis utilizing flash vaporization into a heated reaction chamber, and suggested a pyrolysis mechanism with $CH_3COCH_3 \rightarrow CH_3COCH_2 + H$ as the initiation reaction, based on the product distributions from gas chromatography. Ernst et al. [2] studied acetone pyrolysis using a shock tube and a UV laser absorption diagnostic. They recommended a similar mechanism with a different initiation reaction (R1: $CH_3COCH_3 \rightarrow CH_3 + CH_3CO$). Similarly, Sato and Hidaka [3] investigated acetone pyrolysis and oxidation in a shock tube; they evaluated k_1 by monitoring acetone concentration using laser absorption at 200 nm and 3.39 μm. Saxena et al. [4] performed a direct measurement of k_1 using laser-schlieren. And finally, Pichon et al. [5] developed a detailed kinetic mechanism for acetone, which was validated against their flame speed and ignition delay time measurements.

In contrast to acetone, fewer 2-butanone studies have been performed. Early low-temperature 2-butanone oxidation static reactor studies were conducted by Bardwell and Hinshelwood [6–9]. Decottignies et al. [10] investigated 2-butanone oxidation using laminar premixed methane/air flames doped with different amounts of 2-butanone. Based on the product distributions from gas chromatography, they postulated a kinetic mechanism and suggested three initial decomposition pathways (R2: 2-butanone $\rightarrow C_2H_5 + CH_3CO$; R3: 2-butanone $\rightarrow CH_3 + C_2H_5CO$; and R4: 2-butanone $\rightarrow CH_3 + CH_3COCH_2$), with reaction (3) as the major pathway. Similarly, Serinyel et al. [11] developed a detailed mechanism, which was validated against their shock tube ignition delay times. However, they suggested that reaction (2) is the major initial decomposition channel.

In this work, we present high-temperature pyrolysis studies of acetone and 2-butanone behind reflected shock waves using laser absorption methods to measure time-histories of five species: ketone, CO, CH_3, CH_4 and C_2H_4. These measurements are used to determine decomposition rate constants for both acetone and 2-butanone.

2. Experimental setup

2.1. Shock tube facility

Experiments were performed in the Stanford stainless-steel, high-purity low-pressure shock tube. The shock tube is comprised of a 3.7 m driver section and a 10 m driven section, with an inner diameter of 15.24 cm. Reflected shock temperatures and pressures were determined from the incident shock speed (extrapolated to the value at the end wall) using standard normal shock relations, with an uncertainty of approximately ±0.7% and ±1%, respectively, mainly due to the uncertainty in the measured shock velocity (±0.2%). Helium was used for the driver gas and provided 2–3 ms of high-quality, uniform test time, as evidenced by very flat (±2%) non-reactive pressure traces (see Supplementary data). All laser diagnostics, along with side-wall pressure measurements, were located 2 cm from the driven section end-wall.

Between experiments, the shock tube and mixing assembly were routinely turbomolecular pumped down to ~6 μtorr. Test mixtures were prepared manometrically in a 40 l stainless steel tank heated uniformly to 50 °C and mixed with a magnetically-driven stirring vane for at least 2 h prior to the experiments. Typical mixture compositions from this study were 0.25%, 1% and 1.5% ketone in argon. 99.999% Argon (from Praxair) was used with the ACS spectrophotometric grade acetone (⩾99.5%) and the CHROMASOLV® grade 2-butanone (⩾99.7%) from Sigma–Aldrich. All liquid chemicals were purified using a freeze–pump–thaw procedure to remove dissolved volatiles and air.

2.2. Laser absorption measurements

2.2.1. UV laser absorption of ketones

Ketones are known to have a near UV absorption spectrum, which corresponds to the symmetry forbidden electronic $\pi^* \leftarrow n$ transition [12]. At current experimental conditions, the spectrum is broad and lacking of any fine structures, varying gradually from 220 to 340 nm with peak absorption near 295 nm.

Acetone and 2-butanone were measured at 306.65 nm using the frequency-doubled output of a narrow-linewidth cw (continuous wave) ring dye laser. This system is identical to that used in our laboratory for the detection of OH [13]. Using a common-mode-rejection detection scheme, a minimum absorbance of ~0.2% can be detected, which results in a minimum detection sensitivity of ~200 ppm for acetone and 2-butanone at 1300 K and 1.5 atm. The ketone time-histories are calculated using Beer's law:

$$I/I_o = \exp(-n_{ket}\sigma_{ket}L)$$

where I and I_o are the transmitted and incident laser intensities, n_{ket} is the ketone number density, σ_{ket} is the ketone absorption cross-section, and L is the path length (15.24 cm).The ketone absorption cross-sections determined in separate