Time-resolved carbon monoxide measurements during the low- to intermediate-temperature oxidation of n-heptane, n-decane, and n-dodecane

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ABSTRACT

Time-resolved mid-infrared laser absorption measurements of carbon monoxide were carried out during the low- and intermediate-temperature oxidation of n-heptane, n-decane, and n-dodecane in a shock tube. Dilute mixtures of n-alkane/O_2/Ar were shock heated, initiating oxidation and resulting in CO formation and heat release with time scales of 1 to 10 ms. Experiments are reported in two temperature and oxygen concentration ranges, 686–797 K at 5% O_2 and 1121–1290 K at 0.5% O_2, for pressures around 10 atm. For measurements in the lower temperature range, first-stage ignition was observed and found to exhibit negative-temperature-coefficient behavior. The low-temperature reactivity was found to increase with increasing n-alkane chain length and first-stage ignition delay to be well correlated with literature derived cetane numbers. The time-resolved CO measurements and first-stage ignition delay times provide quantitative targets for kinetic models that are sensitive to important low-temperature ignition chemistry; comparisons are made with n-alkane kinetic models from the literature.

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1. Introduction

Low-temperature heat release (LTHR) and low-temperature ignition is important in many modern combustion engines [1–4]. In spark ignition strategies, LTHR can lead to detrimental engine knock. In modern compression ignition strategies, the compressed gases can be sufficiently low temperature such that the ignition of fuels exhibiting negative-temperature-coefficient (NTC) behavior takes place in two stages, where the magnitude of heat release in the first stage largely governs the second-stage ignition [5]. The importance of LTHR in gas turbines is largely unknown; however, for high pressures the time scales for LTHR become sufficiently short (<1 ms) such that they are comparable to the overall gas turbine combustor flow residence time and LTHR will play a role in both the reacting and transport phenomena that govern turbulent flame dynamics in gas turbines [6–7].

Kinetic modeling studies indicate [5,8–10] that that LTHR is controlled by the addition of molecular oxygen to fuel radicals and the competition between low-temperature chain branching and chain propagating pathways that follows. LTHR leads to the formation of large quantities of carbon monoxide, formaldehyde,

other oxygenated hydrocarbon stables and radicals, and small radical species (e.g., OH). The amount and rate of LTHR plays a crucial role in governing the multi-stage kinetic ignition behavior, in some cases leading directly to hot ignition and in other cases to multi-stage ignition with time scales controlled by the conditions, mixture composition, fuel molecular structure, and physical constraints. Speciation and ignition delays are the primary means by which LTHR is experimentally observed and are presently the basis for constraining and validating kinetic models.

Prior ignition delay studies for pure n-alkanes found in gasoline, diesel, and jet fuels have been carried out in both shock tubes [11–17] and rapid compression machines (RCMs) [18–20] by several research groups. Studies performed in shock tubes have been reported for a range of conditions from high to low temperatures and pressures from atmospheric to those found in engines. Most studies have been isolated to high fuel fractions found in fuel/air mixtures. Fewer studies have reported both first- and second-stage ignition delay times [8,9,12,16,21], in many cases because of the difficulty of isolating first-stage ignition in highly exothermic mixtures.

Time-resolved speciation measurements for large n-alkanes have been reported to a lesser extent than ignition delay. Notable examples of speciation measurements carried out during n-alkane oxidation in shock tubes, include a series of laser absorption studies from Hanson and co-workers [22] who reported measurements

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of OH, H_2O, CO_2, and C_2H_4 during the dilute oxidation (fuel fractions of 100s of ppm) of n-heptane [23], n-dodecane [24], and n-hexadecane [25] at temperatures of 1100–1600 K and pressures of 2–7 atm. Ren et al. [26] and Sun et al. [27] have reported CO measurements made during methyl formate oxidation and acetone pyrolysis at 1–2 atm, respectively; although their studies focused more on the CO diagnostic development and less on combustion chemical kinetics. Campbell et al. [21] also recently reported OH, aldehydes, CO_2, and H_2O laser absorption measurements during the low-temperature (651–823 K) oxidation of n-heptane at 6–7 atm. Other recent work on speciation measurements in shock tubes has been reported by Sajid et al. [28] who measured CH_4, C_2H_2, C_2H_4, during the pyrolysis of n-pentane at high temperatures (1400–2100 K) and atmospheric pressure using mid-infrared laser absorption and Javed et al. [29] who measured CO, CO_2, H_2O, and OH using infrared and ultraviolet laser absorption during the oxidation (1350–1550 K and 2 atm) of gasoline samples and primary reference fuel blends.

Quantitative information under well controlled reaction conditions is needed regarding speciation and first-stage ignition or LTHR to better develop models at low- to intermediate-temperature conditions. Time-resolved speciation measurements have proven to be valuable for developing and validating chemical kinetic models [30]; however, such data from shock tubes is limited at low-temperature combustion conditions and at elevated pressures. Here we present measurements of CO formation under low- to intermediate-temperature conditions during the dilute oxidation of n-heptane, n-decane, and n-dodecane. These measurements provide time-resolved speciation targets and first-stage ignition delay times for the refinement and validation of future kinetic models. Enabled by a sensitive CO diagnostic technique, the present results are unique in that they probe the important low-temperature regime but are carried out at dilute conditions not normally amenable to shock tube studies where larger magnitudes of heat release is often required to observe LTHR. Carbon monoxide is particularly relevant as an indicator of LTHR as its early formation provides LTHR and leads to first-stage ignition and its destruction, leading to carbon dioxide formation, provides the hot second-stage ignition. In this sense, carbon monoxide is an ideal candidate for monitoring and quantifying LTHR. The n-alkanes (C7, C10, and C12) studied here were chosen for their importance as reference fuels or surrogate representatives for gasolines (C7) and jet fuels (C10 and C12). They are also the subject of wide prior kinetic modeling study but yet still the low-temperature oxidation of n-alkanes is a topic of research with unresolved uncertainties.

2. Experimental method

Time-resolved carbon monoxide (CO) measurements were made during the oxidation of dilute n-alkane/O_2/Ar mixtures, following reflected shock heating, at intermediate- to low-temperature combustion conditions. CO was monitored using fixed-frequency mid-infrared laser absorption in the strong fundamental rovibrational band at 4.6 μm. Our approach to CO laser absorption measurements has been described previously in studies where scanned-wavelength [31] and wavelength-modulation spectroscopy [32] approaches were implemented. Here, a simpler fixed-frequency technique is applied with the same hardware previously used.

Experiments were performed in the Rensselaer high-pressure shock tube (internal diameter 5.7 cm, 2.59 m driver, 4.11 driven) described by Wang et al. [33] and Shen and Oehlschlaeger [34]. Incident shock waves were generated via the pressure-induced rupture of polycarbonate diaphragms with tailored N_2/He driver gases to provide extended reflected shock test times. The incident shock trajectory near the driven section end wall (test location) was monitored using a series of fast-response pressure transduc-
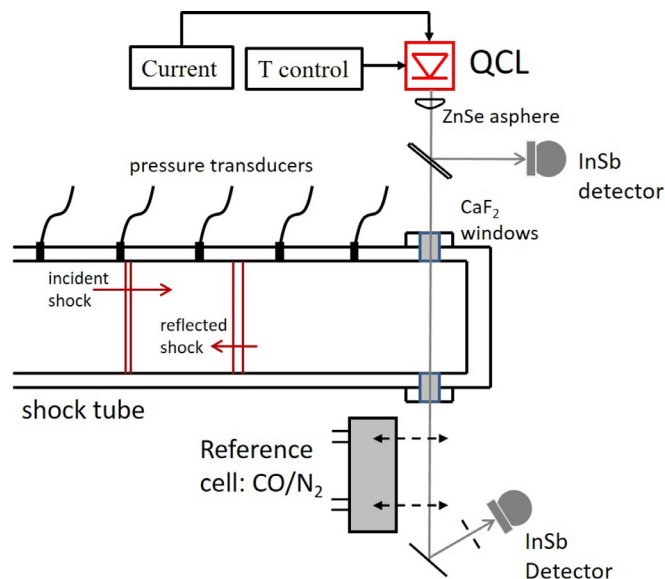

Fig. 1. Schematic diagram of the experimental setup.

ers spaced over the last meter of the driven section and was used to determine the conditions behind both the incident and reflected shock waves using the normal shock relations. Optical measurements were made behind the reflected shock wave at a location 2 cm from the driven section end wall. The shock tube can be uniformly heated using an electric resistance heating systems to provide for the gas-phase study of heavy fuels. In the present study, the driven section was operated at temperatures from 25 to 60 °C.

See Fig. 1 for a schematic diagram of the experimental setup. Mid-infrared laser emission around 4.59 μm was generated using a quantum cascade laser (QCL) from Alpes Lasers (model sbcw1960, linewidth ~10 MHz). The QCL was mounted to a thermoelectric cooler for temperature control and driven by a laser controller (injection current control, ILX Lightwave LDX-3232). The combination of QCL temperature and injection current settings controls its emission frequency and intensity. The QCL emission was collimated with a ZnSe aspheric lens and a portion was sent to a reference detector (LN_2 cooled InSb), used to cancel (normalize) variations in laser intensity, via a beam splitter. The remaining QCL emission propagated through the shock tube (absorption path length = 5.7 cm) to the signal detector (LN_2 cooled InSb), where two flush mounted calcium fluoride windows provided optical access at a measurement location 2 cm from the shock tube end wall. The time history of the CO mole fraction was determined from the measured fractional transmission of laser intensity via the Beer-Lambert law:

$$I/I_0 = \exp(-X_{CO} n_{tot} \sigma L)$$

where I and I_0 are the laser intensity following and prior to absorption, X_{CO} is the CO mole fraction, n_{tot} is the total gas concentration, σ is the absorption cross section of CO at the laser frequency, and L is the absorption path length.

The laser frequency was tuned to the peak of the R(9) CO transition at 2179.7719 cm^{-1} which is sufficiently isolated from interfering water vapor and carbon dioxide absorption. Frequency tuning was manually achieved by varying the injection current to find the peak of the room temperature R(9) CO transition by monitoring absorption within a reference gas cell (CO/N_2) that could be moved in and out of the beam path, as shown in Fig. 1. At high pressures, the R(9) line has some absorption interference from the neighboring R(17) transition (line center at 2179.2438 cm^{-1}) and other surrounding transitions. See Fig. 2 for spectral simulations