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SYNTHETIC-FUEL COMBUSTION; POLLUTANT FORMATION.

SOOT-INITIATION MECHANISMS IN BURNING AROMATICS

THIRD QUARTERLY REPORT

FOR THE PERIOD

1 APRIL 1981 - 30 JUNE 1981

T. TANZAWA, S. P. SCHERTZER and W. T. RAWLINS

PHYSICAL SCIENCES INC.

30 COMMERCE WAY

WOBURN, MA

PREPARED FOR THE

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1. INTRODUCTION

Soot particle formation processes from gaseous hydrocarbon pyrolysis and combustion have been widely studied as shown in the literature reviews by Wagner,¹ Lester and Wittig,² and Palmer and Cullis,³ yet many questions still remain to be solved. In particular, the effects of gas-phase free radicals, such as O and OH, upon mechanisms of formation of incipient soot particles have not been investigated. For experimental observation of the early stages of soot formation, the shock tube technique is uniquely suited since one can achieve physical conditions which are well-defined in comparison with flame experiments. Thus, we have begun an experimental investigation of the kinetics of incipient soot particle formation in a shock tube. As model synthetic fuel compounds, we chose toluene and pyridine. The majority of the data base from previous shock tube studies on the gas-phase kinetics of the soot formation process pertains mostly to pyrolysis, and provides global data. It is well-known that free radicals, such as O, H, and OH, play an important role in aliphatic hydrocarbon combustion;⁴ similarly, they may also have an important role in aromatic hydrocarbon combustion and especially in the fragmentation of ring structures. Furthermore, in combustion of heterocyclic species containing fuel nitrogen (such as pyridine), nitric oxide is formed. All of these species (i.e., O, H, OH, and NO) are amenable to detection using conventional optical spectroscopic techniques.⁵ Thus, combustion experiments monitoring the kinetics of intermediate species and products, in addition to observations of fuel decay and of appearance of incipient soot particles, could provide valuable information on the chemical pathways leading to incipient soot particles and to the major gaseous pollutant, nitric oxide.

During the present reporting period, toluene pyrolysis experiments were carried out using He-Ne laser beam attenuation as a diagnostic for soot formation. In addition, broad-band absorption and emission diagnostics have been set up. In the following discussion, the experimental setups are described in Section 2, and the results of our initial toluene pyrolysis experiments are discussed in Section 3. A progress summary and plans for the next quarter are presented in Section 4.

2. EXPERIMENTAL

The experiments to monitor appearance of incipient soot particles in toluene pyrolysis were carried out in a 4" shock tube which was described in detail in our First Quarterly Report.⁶ In parallel to the toluene pyrolysis study, we performed experiments to characterize incident shock waves, observing density gradients with a laser schlieren technique⁷ and pressure profiles with piezoelectric pressure transducers. The purpose of these experiments was to ensure an undisturbed pressure and density profile during the observation period and to pinpoint the limit of useful observation time. We have also designed and assembled two additional diagnostics: (1) UV absorption by primary aromatic molecules, and (2) visible/UV emission from intermediate hydrocarbon fragments such as C₂.

2.1 Shock Wave Speed Measurement

The speed of the incident shock wave was determined by monitoring the arrival of the shock front at each of four piezoelectric gauges (PCB-- Piezoelectronics Inc., 111-A21) placed at 25.4 cm intervals. The principle of this method was described in our First Quarterly Report;⁶ the electronic circuit used to process the piezo-gauge signals and the idealized expected output signal were shown in our Second Quarterly Report.⁸ Representative piezo-gauge output signals obtained are shown in Fig. 1. It should be noted that the pre-shock noise level was drastically reduced in comparison with earlier piezo-gauge data.⁸ This improvement was accomplished by damping mechanical vibrations of the shock tube with neoprene sheet on the gauge mounts. The shock wave speed is obtained by measuring the time interval (t) between shock wave arrival at consecutive ports; the shock wave speed over each port interval is given by $v = L/t$, where L is 25.4 cm. We consistently observed that attenuation of the shock wave was considerably less than 1% over 1 m; this level of shock attenuation has a negligible effect on the experiments to be undertaken here.

Fig. 1 Representative record for shock wave speed measurement. Point number indicates a $1 \mu\text{s}$ time interval. Conditions behind incident shock wave are $T_2 = 2030 \text{ K}$, $P_2 = 0.43 \text{ atm}$, and $v = 1.40 \text{ mm } \mu\text{s}^{-1}$.

2.2 He-Ne Laser Beam Attenuation Study

The laser used in the soot measurements is a 2 mW CW radiation Model PS2 He-Ne CW laser (TM00 mode, 633 nm) with a beam diameter ($1/e^2$) of 0.8 mm at the aperture exit. The beam is directly focused normal to the shock tube axis. The temporal resolution of the measurement is given by the ratio of the beam diameter to the shock speed and is approximately 0.7 μ s in laboratory time. The laser beam detector is a photodiode operated in the photoconductive mode; the associated electronic amplifier circuit diagram is shown in Fig. 2. A 632.8 nm interference filter (1.0 nm bandwidth) was placed in front of the photodiode to eliminate effects of room light and of emission from the hot gas; an array of diffusers was used to diffuse the small laser beam uniformly onto the photodiode surface. To further eliminate emission from the gas, it was necessary to place a pinhole, slightly larger than the laser beam diameter, at the exit window. Prior to each experiment, the zero-transmittance level is determined by modulating the laser beam. The sensitivity limit of the laser beam attenuation measurement is approximately 0.5% attenuation. The detector output is processed by the CAMAC-PRIME 400 computer data acquisition system described previously.^{6,8}

2.3 Laser Schlieren Study

A series of laser schlieren experiments was performed to test for an unperturbed density profile during the observation period. For this purpose, the diffusers were removed from the exit beam and a knife-edge was positioned to cover the downstream half of the photodiode detector. The principle of the laser schlieren technique⁷ is to utilize the deflection of the beam due to changes in the refractive index brought about by density gradients behind the shock front. The distance between the center of the shock tube and the photodiode is approximately 40 cm. We estimate the sensitivity of the schlieren measurement to be a minimum density gradient of about 5×10^{-5} g/cm⁴, which is sufficient for the purpose at hand.

2.4 UV Absorption and Emission Diagnostics

A UV absorption diagnostic for the measurement of aromatic fuel decay has been designed and assembled. The optical detection system consists of a

Fig. 2 Electronic circuit diagram associated with photodiode in He-Ne laser beam absorption assembly.

deuterium lamp (Optronics Laboratories, Inc. Model UV-40), sapphire windows, a 0.3 m McPherson monochromator (McPherson Model 218) with a grating of 500 nm blaze wavelength, and an RCA 1P28 photomultiplier tube. An optical collimator was placed in front of the 1 mm entrance slit of the monochromator, to yield a time resolution of approximately 2 μ s in laboratory time.

A UV/visible emission diagnostic was also assembled. The detector is an EMI 9813 QA photomultiplier tube powered by an EMI GENCOM Inc., Model 3000R high voltage power supply. An appropriate interference filter and an optical collimator are placed on the shock tube window to obtain a desired wavelength region and approximately 6 μ s (lab time) of time resolution. The outputs of the photomultipliers for the emission and absorption diagnostics are amplified by LeCroy Model 612M Six-Channel Photomultiplier Amplifier and are fed into the LeCroy Model 8210 Multichannel Wave Form Digitizer for acquisition and storage.

3. RESULTS OF HE-NE LASER BEAM ATTENUATION EXPERIMENTS

The appearance of incipient soot particles can be detected by attenuation of a He-Ne laser beam at 633 nm using the experimental setup described in the previous section. This technique has been applied to studies of soot particle formation in aliphatic and aromatic hydrocarbon pyrolysis and combustion.^{9,10,11} Typically, the incipient soot particles, believed to be ~10-30 nm in diameter are assumed to attenuate light according to the small particle limit of Mie theory; this results in a Beer's law relationship between absorptivity and concentration of soot particles:

$$Y = \frac{N_0 \rho_s \lambda}{72\pi L E\{m\} C} \ln \frac{I(0)}{I(t)} \quad (1)$$

where Y is the mass of carbon as soot divided by the total mass of carbon, N_0 is Avogadro's number, ρ_s is the density of soot particles (a value of 1.86 g/cm³ was used), λ is the wavelength of the measurement, L is the inside diameter of the shock tube, C is the total concentration of carbon atoms, and I(t) is the intensity of the transmitted laser radiation as a function of time, t. $E\{m\}$ is the imaginary part of the function $(m^2-1)/(m^2+2)$, where m is the complex index of refraction:

$$E\{m\} = \frac{6nk}{(n^2 - k^2 + 2) + 4n^2 k^2}, \quad \text{where } m = n - ik$$

In Eq. (1), the calculated soot yield is inversely proportional to the function $E\{m\}$. Although experimental and theoretical values of the complex refractive index have been reported for various fuels and combustion environments, most of the reported values are for room temperature. Boynston et al.¹² showed that the absorption coefficient of soot particles deviates drastically from the theoretical predictions above 1700 K. Some representative $E\{m\}$ values from the literature are 0.23 (Dalzell and Sarofim)¹³, 0.19 (Lee

and Tien)¹⁴, and 0.13 (Chippett and Gray).¹⁵ As have been discussed by previous investigators,^{9,10} these numbers are too small and lead to apparent soot conversion efficiencies far in excess of unity. Recent work by Frenklach¹⁶ using a laser Doppler velocimeter indicates that the initially observed particle size is much larger than previously thought, i.e., larger than 30 nm. Obviously, there exists a large uncertainty for the estimation of the absorption coefficient of soot particles. The formation of soot particles may be characterized in terms of the sooting rate which is a function of fuel concentration and total pressure. Thus, in this report, our data will be presented by simply adopting exponents of an empirical relation which Farmer et al.¹⁰ derived:

$$\beta = \tau_{\text{soot}}^{\text{particle time}} [\text{C}_7\text{H}_8]^{.81} [\text{Ar}]^{.14} \quad (2)$$

$$\delta = \frac{\ln(\Delta I/I_o)_{\text{max}}}{t_{\text{particle}}} [\text{C}_7\text{H}_8]^{-1.48} [\text{Ar}]^{-0.24} \quad (3)$$

where τ is an induction time in microseconds for incipient soot particle appearance and $(\Delta I/I_o)_{\text{max}}$ is the slope of a linear part of the beam attenuation profile.

Typical laser beam attenuation profiles for a 1.5% toluene/Ar mixture are shown in Figs. 3 and 4. For the present analysis, the induction time for incipient soot particle appearance was defined as the time between shock front arrival and the intercept of the extrapolated pre-shock transmission level with an extrapolation of the linear part of beam attenuation profile (cf. Fig. 3). For the cases shown here, the attenuation of the laser beam is almost instantaneous on the arrival of shock front. Furthermore, the profile of Fig. 3 is clearly multimodal, with at least three different slopes. This behavior might be an indication of the presence of competing kinetic and/or optical

Fig. 3 Representative laser beam attenuation record for a 1.5% toluene/Ar mixture. Dotted line indicates zero transmission level. Conditions behind incident shock wave are $T_2 = 1750 \text{ K}$, $P_2 = 0.52 \text{ atm}$, and $v = 1.29 \text{ mm } \mu\text{s}^{-1}$.

Fig. 4 Representative laser beam attenuation record for a 1.5% toluene/Ar mixture. Dotted line indicates zero transmission level. 50 mV output from piezo gauge corresponds to 1 psi. Conditions behind incident shock wave are given in Fig. 1. Conditions behind incident shock wave are $T_2 = 2030$ K, $P_2 = 0.43$ atm, and $v = 1.40$ mm μs^{-1} .

processes. For this case, we determined the induction time for each portion of the curve as shown in Fig. 3. The induction time data are compared with those of Farmer et al.¹⁰ in Fig. 5. The agreement between the two studies is excellent over the temperature range 1500 K to 2200 K, despite a considerable difference in pressure range between the two experiments.

It is widely known that the laser beam attenuation experiment to monitor soot particles is often compromised by some light-absorbing intermediate species such as polycyclic aromatic hydrocarbons (PCAH) and their radicals.^{9,17} A laser beam scattering experiment by Graham et al.⁹ showed that no scattering of light was observed at temperatures above 2200 K. However, as shown in Fig. 4, we observe considerable beam attenuation at high temperatures. In view of the results of Ref. 9, it seems unlikely that the attenuation observed at high temperatures can be due largely to soot particles. The high-T attenuation might be due to PCAH and/or radicals of PCAH, since absorption bands of polyphenyl radicals are expected to exhibit a considerable red-shift at high temperatures.¹⁷ Since the absorption coefficients of soot particles or polyphenyl radicals are not known quantitatively, the parameter δ was calculated according to Eq. (3) and plotted as a function of reciprocal temperature as shown in Fig. 6. It should be noted that there is a break point around 1800 K as previous investigators observed in acetylene¹¹ and aromatic hydrocarbon pyrolysis.¹⁰ This is consistent with the hypothesis that two separate processes i.e., fragmentation and polymerization/condensation processes, are competing to form soot at lower temperatures and PCAH fragments at higher temperatures. However, at present our data are too limited in number and scope for such conclusions to be drawn. A more comprehensive data base, with supporting emission and UV absorption measurements (to distinguish soot and PCAH), as well as a more complete test time characterization (see below) are required to substantiate this hypothesis.

In Figs. 3 and 4 the limit of useful test time is difficult to determine from the data. Preliminary calculations for an x-t diagram reported earlier⁶ indicated that the experimental observation time would be about 700 μ s, limited by the arrival of the rarefaction wave. However, an anomalous

Fig. 5 Comparison of our laser beam attenuation induction time data (O) with the least squares line reported by Farmer et al.¹⁰ Pressure dependent induction time data were corrected according to Eq. (2) as discussed in the text. Determinations of three different induction times (τ , τ' , τ'') are shown in Fig. 3.

Fig. 6 Rates of linear part of beam attenuation profiles obtained in this study. Pressure dependences of the rates were corrected according to Eq. (3). Determinations of three different slopes is shown in Fig. 3.

pressure spike is seen at 540 μ s in Fig. 3 and two absorption peaks are seen at 412 and 976 μ s in Fig. 4. These features raise questions about shock stability and uniformity in density behind the shock front. In order to further diagnose this problem, a few laser schlieren experiments were performed, and a representative record is shown in Fig. 7. In Fig. 7, a positive schlieren signal (upper trace) indicates $dp/dx > 0$, i.e., a density increase, where ρ is density and x is distance along the shock tube. The largest schlieren spike indicates the arrival of shock front, which exactly corresponds to the pressure jump (lower trace). Anomalous positive and negative density changes are seen at approximately 425 μ s and 600 μ s after the arrival of the shock front, respectively. It is possible that the former spike is due to the arrival of the contact surface and the latter due to the arrival of the head of the rarefaction wave. However, since the pressure profile is flat and well-behaved for over 800 μ s, the laser schlieren signal is difficult to interpret. In the next quarter, we plan to use visible and infrared emission signatures to completely characterize the shock stability and test times. These measurements will be performed simultaneously with the He-Ne attenuation measurements so that the late-time behavior of the latter can be more readily interpreted. Preliminary results now in hand indicate that the test times are indeed 700-900 μ s, as indicated by the flat portion of the pressure profiles.

Fig. 7 Laser schlieren record in 100% Ar. Conditions are $P_2 = 0.43$ atm, $T_2 = 1500$ K, $v = 1.18$ mm μs^{-1} .

4. PROGRESS SUMMARY AND RESEARCH PLAN

Toluene pyrolysis experiments have been performed using He-Ne laser beam attenuation to monitor soot. The experimental results were consistent with those of previous investigators; however, the laser beam attenuation records showed an anomalously large absorption at the higher temperatures where soot formation should be minimal. This effect could be due to some light-absorbing gas-phase species such as PCAH and/or radicals of PCAH. Diagnostics employed in this report showed ambiguous late-time behavior of the pressure, density, and beam attenuation profiles; clarification of this observation is required.

Plans for the coming quarter are directed toward pyrolysis experiments of toluene and pyridine using He-Ne laser beam attenuation to monitor "soot," UV absorption spectroscopy to detect the reactant and primary products, and visible emission spectroscopy at several wavelengths. The latter part of the coming quarter will be devoted to studies of aromatic combustion. In preparation for the combustion experiments, we will assemble diagnostics and carry out calibration experiments for CO-O flame band emission, CO and CO₂ IR emissions, and UV resonance absorption by NO and OH.

The program accomplishments to date are reasonably consistent with the original program schedule, and no major difficulties have been encountered. Contributing technical personnel during this quarter were T. Tanzawa, S. P. Schertzer, R. H. Krech, and W. T. Rawlins.

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