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MASTER

SOOT FORMATION FROM POLYCYCLIC AROMATICS

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ABSTRACT

The initial phase of this study has been focused on determining the accuracy of the absolute values of soot conversion and the reliability of the experimental techniques employed to determine soot formation from polycyclic aromatics in various shock tube experiments. The LSU experimental results have demonstrated consistency between the present observations and results reported by other research groups, thus eliminating the "controversies" suggested by a number of researchers.

Analysis of the preliminary experimental data has resulted in the postulation of a new conceptual mechanistic model for soot formation from polycyclic aromatics. Preliminary analysis using the model offers an explanation of various experimental trends. Additional work with this conceptual model may subsequently lead to a more systematic approach for determination and classification of the soot formation data.

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I. INTRODUCTION

Perhaps the most important questions that have been raised recently¹ with regards to shock tube data on soot formation are concerned with the absolute values of soot conversion and the reported maximum soot yield observed at temperatures near 1800°K. The development of answers to these questions are of great practical and theoretical importance. Therefore, the initial phase of this program was focused on resolving these issues.

Approximately 5 years ago Graham and co-workers^{2,3} investigated soot formation from a number of polycyclic aromatics. These experiments were carried out behind incident shock waves and a pronounced maximum in soot conversion was observed near 1800°K. Complete conversion of fuel carbon to soot was assumed at the maximum point.

Similar experiments conducted at LSU^{4,5} behind reflected shock waves confirmed the existence of a maxima for soot production as a function of temperature. Using the dispersion equation of Stull and Plass⁶ the maximum conversions were estimated to be approximately 80%. Even though the agreement between these two studies was good, at least in a qualitative sense, the question has been raised⁷ whether the observed maxima are "real" or are just a "shock-tube" effect since in the case of acetylene no such maximum has been observed².

The estimation of absolute soot concentrations based on laser absorption techniques, employed both by Graham and co-workers and at LSU, has also been questioned due to ambiguities in the optical properties of soot particles. The latest results indicate that the accuracy of this measurement technique for soot conversion determinations is well within

a factor of 2-3⁸. Recent results obtained by Kern, with whom we have been in close communication (see section VI), led him to suspect the order of magnitude of the soot conversion values reported in the laser absorption studies. Kern reported⁹ that the mass balance of the species produced behind reflected shock waves near 1800°K which were monitored by a time-of-flight mass spectrometer could not account for any significant quantity of soot production. His experimental conditions were quite similar to those previously reported at LSU: nearly the same initial concentration of toluene; but somewhat lower initial pressure which was assumed to be of minor importance due to earlier results^{4,5}. Another recent shock-tube study¹⁰ reported a different dependency of soot formation on the initial concentration of fuel.

In light of these concerns, the initial phases of the present study were designed to investigate these apparent differences and determine the reliability of the laser absorption technique for shock tube soot concentration measurements.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

The experiments have been conducted in a conventional stainless steel shock tube: 7.62 cm i.d., 3 m driver section and 7.3 m driven section. Both mechanical and diffusion pumps were used in the shock tube gas handling and vacuum system. The systems could be evacuated to less than 1×10^{-5} torr. The mixtures of gases were prepared manometrically and allowed to mix for at least 24 hours prior to experimental runs. MCB reagent grade toluene, purified by repeated freezing and evacuation, and Matheson helium (99.995%) and argon (99.995%) were used in this study.

The state of the gas behind the reflected shock wave was calculated in a standard manner¹¹ using the measured incident shock velocity extrapolated to the end wall of the shock tube. Shock velocities were measured using four piezoelectric pressure transducers to trigger the start and stop channels of an interval timer. The observed shock waves attenuation was approximately 2% per meter.

The soot conversion was determined from attenuation of the beam from a 15 mw cw He-Ne Spectra-Physics Laser monitored by either an IP28 (6328 Å) or by an ISV-369A (3.39µm) photomultiplier. Output signals from the photomultipliers and the pressure transducer located at the optical observation station were displayed on a Nicolet Explorer Digital Oscilloscope.

The fractional conversions to soot were calculated from the Rayleigh limit of Mie theory using $(1.834 - 0.825i)$ for the complex refractive index⁴ of soot.

Careful alignment and adjustment of the optical system at 6328 Å resulted in an excellent signal-to-noise ratio of the absorption signal. Preliminary test-runs with the modified facilities were in good agreement with previously reported soot yields^{4,5}.

The design of the optical system at $3.39\mu\text{m}$ was optimized so that emission was only a negligible component (less than 0.1%) of the absorption signal. This was achieved by using the laser beam of the maximum power, a narrow-band interference filter centered at $3.39\mu\text{m}$ and a number of optical stops.

III. EXPERIMENTAL RESULTS

A. Low-Pressure Experiments

Two series of experiments with toluene-argon mixtures were carried out: the first, 0.311% of toluene, at conditions similar to the previous LSU experiments and the second, 1.75% of toluene, at conditions similar to Kern's work. Soot was monitored by laser-absorption at $6328 \text{ \AA}$ and the initial conditions are summarized in Table 1.

The data obtained in the first series of experiments for both induction times, see Figure 1, and soot conversions, see Figure 2, were in excellent agreement with the previous results obtained at LSU. However, comparison of the results from the first and second series of tests, which were carried out at the same initial concentration of toluene but at different pressures, indicated a somewhat unexpected behavior. The measured low pressure induction times were predicted well by the same empirical expression obtained at the high pressures (Fig. 1). However, the low pressure soot conversions exhibited a much stronger pressure effect than had been previously reported at higher pressures. The results shown in Figure 2 indicate that the soot conversion maximum is shifted towards higher temperatures at low pressures. In Figures 3 and 4, soot conversions vs. temperature are plotted for a number of experimental observation times. These results indicate that the maximum soot conversion is not only a function of temperature but also of observation time for a given initial fuel concentration.

Analysis of these results indicates that there is no longer any controversy between Kern's results and the LSU results over the order of magnitude of soot conversion if account is taken for the observed pressure effect and the fact that the observation times in Kern's experiments were no longer than 1.2 msec^9 .

TABLE 1. Experimental Conditions for Soot Formation Studies Based on Light Absorption at 6328 Å.

Initial Conditions \ Mixture		0.311% Toluene + Argon	1.75% Toluene + Argon
T_5	(°K)	1437 - 2239	1655 - 2347
P_5	(atm)	1.80 - 2.87	0.30 - 0.52
C_5	(mol·cm ⁻³)	(1.53 - 1.57)*10 ⁻⁵	(2.24 - 2.71)*10 ⁻⁶
[Carbon] ₅	(atoms·cm ⁻³)	(2.01 - 2.07)*10 ¹⁷	(1.65 - 2.00)*10 ¹⁷

Figure 1: Induction times in toluene-argon mixtures monitored at 6328°A.

Figure 2: Fractional conversion to soot in toluene-argon mixtures monitored at 6328°A.

Figure 3: Fractional conversion to soot monitored at 6328°A.

1.75 % Toluene + Argon

$P_1 = 5.0$ Torr

Figure 4: Fractional conversion to soot monitored at 6328°A.

The absolute accuracy of soot conversion values, which is known to be strongly dependent on the optical properties of soot, has not been clarified to date. For example, if the complex refractive index for soot particles at $6328 \text{ \AA}$ derived from recently reported dispersion model of Lee and Tien¹² is utilized in analyzing the present data, a maximum soot conversion of 121 percent is obtained.

B. IR Measurements

Absorption of a laser beam at $3.39 \mu\text{m}$ was measured in a series of experiments with 0.311% toluene in argon carried out at $(2.01 - 2.06) \times 10^{17}$ atoms C/cm^3 between 1488 and 2057°K . As expected^{2,3} the induction times obtained were longer than those determined by attenuation of the laser beam at $6328 \text{ \AA}$ (Fig. 5). It is interesting to note, however, that the ratio of the measured induction times at $3.39 \mu\text{m}$ and $6328 \text{ \AA}$ is approximately constant. This result may imply that consecutive types of reactions are involved in the soot formation process.

The present results on soot conversion obtained at $3.39 \mu\text{m}$ are similar to those obtained at $6328 \text{ \AA}$ with regards to the dependency on temperature and the observation time and position of the maximum. However, in some cases the predicted carbon conversion overshoots 100%. This overshoot beyond 100% conversion may be due to the assumption that the soot particle size is less than $500 \text{ \AA}$ which leads to the Rayleigh limit of the Mie scattering theory. If the particle size is actually larger than $500 \text{ \AA}$, the dependency of optical properties of the soot on the particle size must be taken into consideration.

Graham, et al², assuming a coagulation model for sticky particles, deducted that soot particles do not grow larger than $400 \text{ \AA}$. Recently, Bro, Wittig and Sweeney¹³ reported the growth of soot particles up to

Figure 5: Induction times in toluene-argon mixtures at $[\text{C}]_5 \approx 2.10^{17} \text{ atom/cm}^3$.

1000 Å during the pyrolysis of acetylene behind reflected shock waves. In an attempt to resolve the question of particle size, an experimental program utilizing light scattering experiments has been initiated. This work is discussed in the next section.

C. Light Scattering Experiments

Preliminary experiments have been carried out in an effort to determine the soot particle size by applying frequency shifted laser doppler velocimetry. The advantages of using this technique are:

1. frequency shift allows monitoring of stationary particles;
2. high spatial resolution of scattering;
3. high sensitivity due to heterodyne detection;
4. simultaneous absorption measurements do not require additional laser;
5. availability of commercial equipment.

A TSI Model 9100-3 general purpose LDV system was employed in these studies. Briefly (see Figure 6), the beam from a 15 mw He-Ne laser is divided into two parallel beams by a beamsplitter. One of the beams is passed through the Bragg cell (TSI Model 9182) where its frequency is shifted by 40 MHz and subsequently both beams, shifted and unshifted, are focused onto the center of the shock tube by a transmitting lens (120mm focal length). The shock tube windows were made from the high quality fused quartz, Suprasil-1.

The scattered light from the particles is focused onto a photomultiplier tube (TSI Model 9142) and its output is downmixed (TSI Model 9186), filtered (TSI Model 1984), and displayed on the digital oscilloscope.

Figure 6

(a) LDV SYSTEM IN FORWARD SCATTER MODE

(b) SCHEMATIC OF OPTICAL SYSTEM

Preliminary experiments indicated that the soot particle size was large enough for scattering to be detected by this technique (Fig. 7). Since this method has not been previously reported in conjunction with shock tube measurements, preliminary studies employing seeded flows behind reflected shock waves were conducted in order to avoid any possible errors in analysis and interpretation of the data.

A technique for effectively introducing the particles into the shock tube was developed in our laboratory by employing a trial and error approach. Figure 8 shows a schematic diagram of the seeding system which was developed. The main feature of the seeding system is the on/off mechanism of a toggle valve which allows particles to be introduced into the shock tube. The valve is mounted on a detachable plug (for easy cleaning) which is inserted and screwed into the shock tube wall. A 1/16" bore is drilled inside the plug which acts as an injector for the seed particles. During the seeding operation a high vacuum is pumped on the shock tube side of the system, and particles are loaded into the other side of the toggle valve. A high vacuum is then slowly drawn on the particles in such a way that the particles are not sucked back into the vacuum system. When the desired pressure is reached, the vacuum pump is isolated from the system and argon is introduced into both the shock tube and the line containing the particles. The pressure in the line is set to a higher value (about 1 atm.) than the pressure in the test section of the shock tube. Due to the high pressure difference between the inside of the line and the shock tube, particles are sucked and dispersed uniformly into the shock tube upon opening the toggle valve. The toggle valve is closed immediately afterwards and while the

a

b

Figure 7: Scattering from soot particles
a) behind reflected shock wave
b) few seconds after the run

Figure 8

SCHEMATIC DIAGRAM OF PARTICLES SEEDING DEVICE

particles are still floating inside the shock tube, an experiment with the LDV system is carried out. Approximately ten to fifteen minutes are required for the particles to settle to the bottom of the shock tube after the toggle has been opened.

Preliminary experiments with argon seeded by Kaolin particles were carried out, and typical results are presented in Figures 9a and 9b. Prior to shock arrival the quality of the signal is good and analysis of the frequency indicates that particles are stationary. However, after the reflected shock wave passes the observation station, the quality of the signal is poor even though a good burst can occasionally be observed (see Fig. 10). The Doppler frequency of these rare bursts indicates that particles are moving outwards from the end plate. This may be a significant observation. Nevertheless, the quality of the signal must be improved prior to making any useful measurements.

One of the possible difficulties in the preliminary experiments may be due to the choice of particle type since the Kaolin particles may possibly disintegrate by shock compression. Additional experiments employing Al_2O_3 particles are in progress.

a

b

Figure 9: a) upper beam - LDV signal in seeded flow.
lower beam - pressure trace
b) expanded upper beam of a.

Figure 10: Occasional LDV signal behind reflect shock wave.

IV. DISCUSSION

The experimental soot conversion data obtained to date demonstrate that the position of the maximum of soot conversion is not universal, but rather is dependent on a combination of experimental conditions, including temperature, pressure, concentrations and observation time. This behavior provides a strong indication that the soot formation process for aromatic hydrocarbons is dominated by kinetic processes rather than equilibrium considerations.

To date the only hypothesis advanced to explain the existence of the soot formation maximum has been proposed by Graham et al.². These authors have suggested that the competition between two parallel reaction pathways, condensation and fragmentation, is responsible for the phenomena. According to their scheme,

an increase in fragmentation will decrease the amount of soot formed via the fast, direct route.

The fragmentation process is probably determined by the unimolecular decomposition of the parent hydrocarbon. For example, the following sequence of reactions has been recently proposed for the decomposition of toluene¹⁴.

Under the conditions of the present shock tube experiments, the decomposition of toluene is within the fall-off region¹⁴. If fragmentation reactions are important for the overall soot formation process, it is possible to expect a stronger pressure effect on soot yield at lower pressures. However, according to Graham's model, lowering the pressure will reduce the rate of fragmentation and hence enhance the soot production through the condensation path. This expectation is contradictory to present observations.

Based on these observations and the fact that the fastest reactions during induction periods are usually radical-reactant reactions, we hypothesize that the main route for soot formation from polycyclic aromatics must involve the interaction of some type between the active decomposition products and the aromatic ring. Consider the following formal scheme:

where A denotes the aromatic hydrocarbon and R generalizes the active decomposition and fragmentation products. The decomposition reaction is a unimolecular process and therefore it has a high activation energy (of the order of 100 kcal/mol¹⁴). The apparent activation energy of R2 is expected to be relatively low since the overall temperature dependence of the induction period for soot appearance is approximately 30-40 kcal/mol^{4,5}. The latter conclusion may suggest the chain character of process R2 that will be referred to as "polymerization".

The analysis of the proposed scheme may offer an explanation for various experimental observations on soot formation.

a) The dependence on temperature. At low temperatures when decomposition is slow, process R2 is also slow due to the low concentration of the active intermediates, R. An increase in temperature, increases the rate constants of both decomposition and polymerization, and also increases their ratio in accordance with the difference in activation energies which results in higher concentration of R. Hence the overall process R2 is enhanced. However, as the ratio of the rate constants increases further, the decomposition process also begins to influence the product term, $[A] \cdot [R]$, by lowering the concentration of the parent hydrocarbon. This slows down the soot formation rate via R2 after the initial period of acceleration. Thus, when compared at the same observation time, the soot conversion must pass through a maximum with an increase in temperature while the position of the maximum is determined by the ratio of decomposition and polymerization rates

$$\gamma = \frac{k_d[A]}{k_p[A] \cdot [R]} = \frac{k_d}{k_p[A]^\alpha}$$

where k_d and k_p are the rate constants of the decomposition and polymerization processes, respectively, and α has a positive but not necessarily constant value.

b) The dependence on pressure. When compared at the same temperature, the decrease in pressure will decrease the rate of decomposition and hence the rate of soot production must decline. In other words, the maximum will be shifted towards higher temperatures and the extent of this effect will depend on the pressure itself according to the fall-off behavior.

c) The dependence on the initial concentration of aromatic hydrocarbon. A decrease in the initial concentration of A at constant temperature and pressure will have the same effect on ratio γ , given by expression (1), as an increase in temperature at constant concentration and pressure that was discussed in part a. Suppose that the soot conversion is maximum when ratio (1) equals γ_c . At low initial concentrations of A, when $\gamma > \gamma_c$, an increase in the concentration will decrease the value of γ and hence increase the soot production whereas the opposite effect will be observed in the range where $\gamma < \gamma_c$.

Such behavior may explain the "contradiction" over the different concentration effects suggested by Vaughn¹⁰ since the concentrations used in his work were higher by an order of magnitude than those employed in the previous study^{4,5}.

Recently, Vaughn¹⁰ and Kern⁹ have observed the increasing formation of acetylene and polyacetylenes at conditions of ring rupture that may also support the scheme hypothesized earlier. Vaughn¹⁰ also observed the formation of benzene. Based on these results the following mechanistic scheme is proposed:

where B generalizes various aromatic compounds. This scheme will have the same characteristics as the one discussed earlier but it may also incorporate soot formation from acetylene, for example via:

Thus we hypothesize that soot formation from acetylene and aromatic hydrocarbons involves more or less similar polymerization paths but different initiation processes.

V. CONCLUSIONS AND THE RESEARCH PLAN

The proposed mechanistic scheme for soot formation offers an explanation for various experimental observations which previously could not be qualitatively explained. Thus, work during the next six months will be directed towards further development of the proposed scheme and will include:

1. Experimental studies of soot formation (soot conversion and induction times) from acetylene, benzene (or toluene) and their mixtures.
2. Theoretical development of the scheme in order to relate the model parameters with observed quantities.
3. Further experimentation with LDV in an effort to determine particle sizes and growth rates.

VI. INTERACTIONS

Regular contacts with Dr. Kern's research group at the University of New Orelans will be maintained. Their time-of-flight mass spectrometer-shock tube experimental facilities can be used for the identification of certain intermediate species that will compliment our study of overall kinetic parameters. Our results, in turn, will help them to focus their attention on particularly important experiments and choose experimental conditions which will optimize the usefulness of their data.

VII. PROFESSIONAL PERSONNEL

Professor M. Frenklach	-	principal investigator
Professor R. Matula	-	participating faculty
Dr. S. Taki	-	research associate
C.K. Li Kwok Cheong	-	graduate student (M.S.)

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