

## A Conceptual Model for Soot Formation in Pyrolysis of Aromatic Hydrocarbons

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Soot formation in toluene-argon mixtures has been investigated behind reflected shock waves by monitoring attenuation of a laser beam in both the visible (632.8nm) and the infrared (3.39  $\mu\text{m}$ ) regions of the spectrum. The experiments were carried out at nearly constant total carbon atom concentration over temperature and pressure ranges of approximately 1500–2300K and 0.03–0.3 MPa, respectively. The experimental data indicate that there is a strong pressure effect on soot formation at lower pressures. The bell-shaped dependence of soot conversion on temperature shifts toward higher temperatures with decreasing pressure. The observed phenomenon can not be rationalized within Graham's model. A new conceptual model for soot formation is proposed that not only explains the current results but also unifies the various experimental facts which previously had been considered to be contradictory. The ratio of induction times for soot appearance in the visible and infrared regions was observed to be approximately constant over a wide temperature range, which is also in harmony with the proposed model.

### INTRODUCTION

Soot formation in practical combustion systems has become one of the major topics of current research activities in combustion. Over the years many experimental facts have been accumulated and a variety of phenomenological models of soot formation has been suggested [1–3]. The overall understanding of the soot formation mechanism, however, remains unclear. Even in the case of homogeneous pyrolysis of aromatic hydrocarbons, which is probably the simplest situation, there is no general agreement on the empiricism associated with incipient soot formation.

Approximately seven years ago Graham and co-workers [4, 5] investigated soot formation from a number of aromatic hydrocarbons. Their experiments were carried out behind incident shock waves and they monitored soot formation by attenuation of a laser beam. A pronounced maximum in soot yield was observed near 1800K. Complete conversion of fuel carbon to soot was assumed at the maximum point.

Similar experiments behind reflected shock waves [6, 7] confirmed the existence of a maximum for soot production as a function of temperature. By the dispersion equation of Stull and Plass [8], the maximum conversion of carbon atoms to soot was 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 raised [9] whether the

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observed maxima were "real" or were just "shock-tube" effects.

In a recent shock tube study, Vaughn et al. [10, 11] have employed gravimetric techniques to measure soot formed during the pyrolysis of benzene. They reported that soot conversion increases up to 80% at 1900K and remains constant at higher temperatures. The authors have noted, however, that the amount of soot measured at higher temperatures depended on the waiting time between termination of the experiment and gravimetric analysis.

The order of magnitude of the absolute values of soot formation reported in the laser absorption studies [4-7] has been questioned by Kern. Recent results of Dyer and Flower [12] have indicated that the accuracy of the optical technique is within a factor of 2-3. Kern [13], however, reported that a mass balance of the species produced behind reflected shock waves near 1800K, 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 by Wang et al. [6, 7]: nearly the same initial concentration of toluene; but somewhat lower initial pressure, which was assumed to be of minor importance due to earlier results [6]. There is also no agreement upon how soot yield depends on the initial concentration of fuel. Wang et al. [6] observed positive effect—more soot is formed at higher concentrations—whereas the opposite was reported by Vaughn [11].

All of the various experimental results described above can be consistently explained in terms of the conceptual model for soot formation from aromatic hydrocarbons presented in this paper.

## EXPERIMENTAL

The experiments have been conducted behind reflected shock waves 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 systems. The systems could

be evacuated to less than  $1 \times 10^{-5}$  Torr. Mixtures of toluene highly diluted in argon were prepared manometrically in a stainless steel tank and allowed to mix for at least 24 h 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 manner [14] 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 wave attenuation was approximately 2%/m.

The soot conversion was determined by measuring the attenuation of the beam from a 15 mw cw He-Ne Spectra-Physics laser which was operated either in the visible (632.8 nm) or in the infrared (3.39  $\mu$ m) region of the spectrum. The absorption was monitored by an IP28 (in visible) or ISV-369A (in infrared) photomultiplier. Output signals from the photomultiplier and the pressure transducer, located at the optical observation station, which was positioned approximately 10 mm from the end wall of the shock tube, were displayed on a Nicolet Explorer III digital oscilloscope. Careful alignment and adjustment of the optical system at 632.8 nm resulted in an excellent signal-to-noise ratio of the absorption signal.

The design of the optical system at 3.39  $\mu$ 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 at maximum power, a narrow-band interference filter centered at 3.39  $\mu$ m, and a number of optical stops.

## RESULTS

Two toluene-argon mixtures were studied. The first mixture, 0.311% of toluene, was tested at conditions similar to those reported by Wang et al. [6, 7] and the second mixture, 1.75% of toluene, was studied at conditions similar to those reported by Kern [13]. The experimental condi-

TABLE 1  
Experimental Conditions

Mixture	Percent (vol.) of toluene in argon	Absorption mode	$T_5$ (K)	$P_5$ (MPa)	$C_5 \times 10^3$ (kmol/m <sup>3</sup> )	$[\text{Carbon}]_5 \times 10^{-23}$ (atoms/m <sup>3</sup> )
1	0.311	Visible	1437-2395	0.183-0.306	15.3-15.8	2.01-2.07
1	0.311	Infrared	1601-2211	0.207-0.287	15.3-15.8	2.01-2.07
2	1.75	Visible	1655-2347	0.0308-0.0529	2.24-2.71	1.65-2.00

tions, summarized in Table 1, were chosen so that the initial concentration of toluene was approximately the same in all runs but the pressure behind the reflected shock wave,  $P_5$ , was varied by approximately a factor of six.

For each mixture a series of experiments was carried out in which soot formation was monitored by measuring the attenuation of the laser beam in the visible region of the spectrum. The first mixture was also tested in the infrared. A typical experimental record is shown in Fig. 1. Inspection of these results indicates that absorption is increasing even after the expansion wave arrives at the observation station. This indicates that a considerable amount of soot can be formed during the cooling period when the total density is decreasing and, as a consequence, the gravimetric approach [10] probably overestimates soot yields.

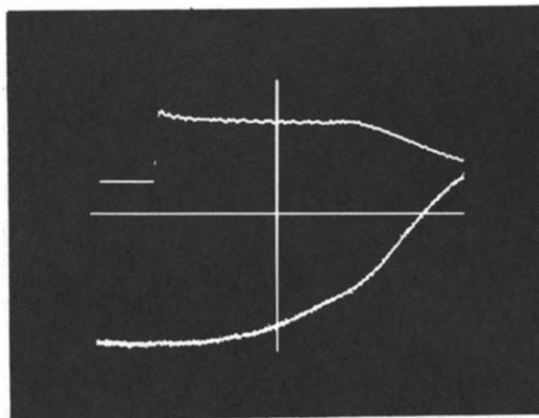


Fig. 1. A typical experimental record ( $T_5 = 1495\text{K}$ ,  $P_5 = 0.193\text{ MPa}$ ) showing that the absorption continues to rise (lower trace) even after expansion wave arrival signaled by sudden reduction in pressure (upper trace).

Evaluation of the absolute values of soot conversion constitutes a problem at the present time. Indeed, if the complex refractive index for soot particles derived from the recently reported dispersion model of Lee and Tien [15] is utilized in analyzing the absorption data, maximum soot yields exceed 100% for both the visible and infrared experiments. This apparent paradox is probably due to the fact that in analyzing the data it has been generally assumed that particle size is below the Rayleigh limit, while in reality the soot particles are likely to be larger than the Rayleigh limit [16, 17]. In the present study, fractional carbon atom conversions to soot were calculated according to Graham's model [4, 7], but they are presented in a somewhat arbitrary form, as percent soot yield multiplied by  $E(m)$ , designed to emphasize this unresolved ambiguity and the uncertainty in the value of  $m$  as well. The quantity  $E(m)$  appearing in Figs. 2-5 is defined as  $E(m) = -\text{Im} [(m^2 - 1)/(m^2 + 2)]$ , where  $m$  is the complex refractive index of soot particles [4].

Figure 2 presents the results of the first series of experiments. The S-shaped character of the time dependence of soot yield and its evolution with temperature were typical for all three series of experiments. Soot conversion displayed versus temperature at a given time passes through a maximum and, as shown in Fig. 3, the temperature corresponding to the maximum and the magnitude of the maximum are dependent on the observation time. Determination of soot yields by absorption measurements in the infrared region of the spectrum (see Fig. 4) indicated slightly higher conversion, with the maximum yield shifting to higher temperatures.

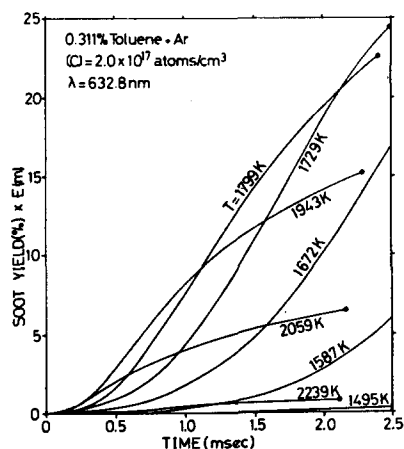


Fig. 2. The time history of the soot formation.

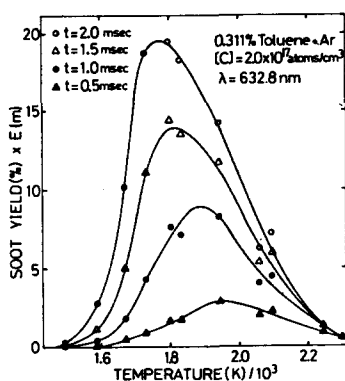


Fig. 3. The maximum soot yield is shifted to lower temperatures at longer observation times.

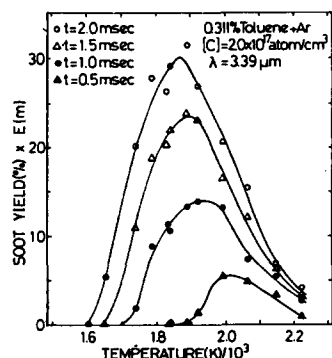


Fig. 4. The soot yield "bells" are shifted to higher temperatures at longer wavelength.

The experimental results obtained at 632.8 nm with mixtures one and two, where the initial total carbon atom concentration was maintained constant but  $P_5$  was varied by approximately a factor of six, are shown in Fig. 5. Inspection of these results indicates that at low pressures the measured soot yields are shifted to higher temperatures. The observed pressure effect is much stronger than would have been expected from the previously reported high pressure results [6]. Thus, in the vicinity of the high-pressure maximum, the soot yields at low pressures are very small. This leads to the conclusion that the pressure shift and the short dwell time ( $\sim 1$  ms) may account for the substantial differences between the soot yields reported by Kern [13] and those reported earlier in conventional shock tube studies [4-7].

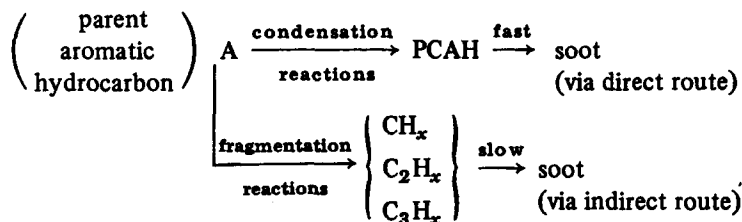
In the present studies, the experimental induction time for soot appearance was defined by the point of maximum curvature in the absorption signal. The present soot induction time data at both pressures (see Fig. 6), which were obtained at 632.8 nm, are in excellent agreement with the empirical expression reported by Wang et al. [6, 7]. The soot induction times observed in the infrared were longer than those measured in the visible region of the spectrum (see Fig. 7). Inspection of Fig. 7 indicates that the ratio of the two induction times is approximately constant over the temperature range tested.

## DISCUSSION

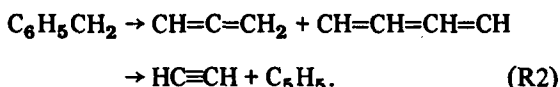
The present experimental results demonstrate that the position of the measured maximum in soot yield is not universal, but rather is dependent on experimental controllable variables including observation time (Fig. 3) and total pressure (Fig. 5), as well as the wavelength employed in the measurement (Figs. 3 and 4). 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. [4]. These authors suggested that the competition between two parallel reaction pathways, condensa-

**nomenon.** According to their scheme,



Fragmentation is probably controlled by unimolecular processes associated with the parent ring. For example, the following sequence of reactions has been proposed as part of the decomposition mechanism for toluene [18, 19]:



$\lambda = 632.8 \text{ nm}$   
 $\circ$  0.311% Toluene-Ar  
 $[C] = 2.0 \times 10^{17} \text{ atoms/cm}^3$   
 $\triangle$  1.75% Toluene-Ar  
 $[C] = 1.65 \cdot 2.0 \times 10^{17} \text{ atoms/cm}^3$   
 — Wang et al.

the rate of fragmentation and hence enhance the soot production via the condensation or fast direct route. This expectation based on Graham's model is contradictory to present observations.

TIME = 1.5 msec  
 $\lambda = 632.8 \text{ nm}$   
 $\bigcirc - 0.311\% \text{ Toluene} \cdot \text{Ar}, [\text{C}] = 2.0 \times 10^{17} \frac{\text{atoms}}{\text{cm}^3}$   
 $\triangle - 1.75\% \text{ Toluene} \cdot \text{Ar}, [\text{C}] = 1.65 - 2.0 \times 10^{17} \frac{\text{atoms}}{\text{cm}^3}$

SOOT YIELD (%)  $\times$  E(m)

TEMPERATURE (K) /  $10^3$

$P_5 = 0.25 \text{ MPa}$   $P_5 = 0.04 \text{ MPa}$

0.311% Toluene-Ar  
 $[C] = 2.0 \times 10^{17}$  atoms/cm<sup>3</sup>

- 3.39  $\mu$ m
- 632.8 nm

— Wang et al.  
 632.8 nm

Fig. 7. The induction times in the infrared are longer than those in the visible, and their ratio is approximately constant over the temperature range studied.

evolution of this shape with increasing temperature, that is, acceleration of the initial phase but a decrease in the final conversion, suggests the following kinetic skeleton:



where  $A$ ,  $X$ , and  $S$  denote initial reactant, intermediate species, and final product, respectively. The amount of  $S$  formed at time  $t_{\text{obs}}$  is given by

$$[S] = \int_0^{t_{\text{obs}}} \{\text{rate of (R4)}\} dt \\ = \int_0^{t_{\text{obs}}} k_p[A][X] dt. \quad (1)$$

Qualitatively, the numerical value of the concentration of  $S$  can be analyzed in the following manner. When reaction (R3) is slow, reaction (R4) is also slow due to the low concentration of intermediate  $X$ . Increasing the rate of reaction (R3) by means of its rate constant  $k_f$  enhances production of  $X$  and hence increases conversion to  $S$ . However as  $k_f$  is increased further, reaction (R3) also begins to influence the product terms  $[A] \times [X]$ , by lowering the concentration of reactant  $A$ ; this slows down production of  $S$  via reaction (R4) after the initial period of acceleration. Thus, when compared at the same observation time, the yield of  $S$  passes through a maximum as  $k_f$  is increased.

The numerical results obtained for the conversion of  $A$  to  $S$  as a function of characteristic parameters associated with the kinetic skeleton are given in Fig. 8. The characteristic parameters utilized in these computations are given by

$$r = k_f/k_p[A]_0, \quad t^* = 1/k_p[A]_0. \quad (2)$$

The abscissa in Fig. 8 is expressed in terms of the dimensionless ratio  $r$ , but the maximum itself can only be obtained when the numerator of  $r$ ,  $k_f$ , is varied. A maximum can not be ob-

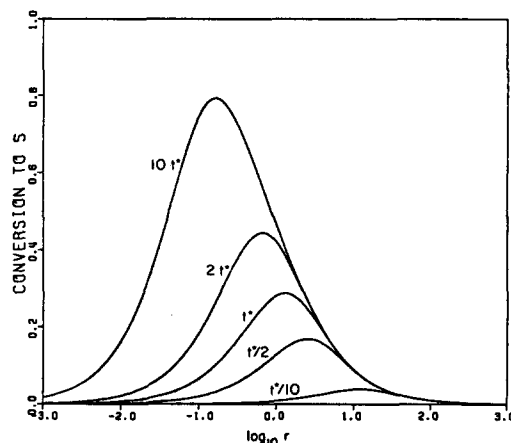


Fig. 8. The computed profiles of the conversion of  $A$  to  $S$  exhibit trends similar to experimental soot yields. The observation times are given in terms of  $t^* = 1/k_p[A]_0$  (see text).

tained when either  $k_p$  or  $[A]_0$  is varied. Mathematically this result becomes clear since as the integrand in Eq. (1) increases the numerical value of the integral also increases. Phenomenologically, for a fixed time scale of reaction (R3), an increase in the number of binary collisions accelerates (R4) and increases the conversion to the final product.

Another distinctive feature of the skeleton scheme is that at infinite time it yields kinetically frozen concentrations for both  $X$  and  $S$ . This kinetically frozen composition is a monotonic function of the ratio  $r$ .

If one associates  $A$  and  $S$  in the skeleton scheme with intact rings and soot respectively, the similarity of Figs. 3 and 8 can be rationalized if reaction (R3) models a rate-limiting step in the decomposition of the parent aromatic hydrocarbon and reaction (R4) generalizes the main route of soot formation, which presumably has a chain character and will be referred to as "polymerization." The decomposition of the ring is a unimolecular process, and therefore it has a high activation energy (of the order of 400 kJ/mol) [18]. The apparent activation energy of chain process (R4) is expected to be relatively low since the overall temperature dependence of the induction period for soot appearance is approximately 150–200 kJ/mol [7, 20]. An increase in temperature

increases both the rate constants of the decomposition,  $k_f$ , and the polymerization,  $k_p$ . However, due to the relative magnitudes of the activation energies,  $r$  will increase with temperature. Increasing the ratio  $r$  primarily by varying  $k_f$  satisfies, according to the earlier discussion, the condition required to obtain a maximum in the yield of  $S$  of the skeleton scheme.

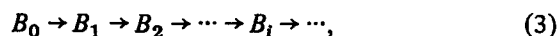
The dependence of soot yield on pressure (Fig. 5) can be readily explained with this conceptual kinetic model. A decrease in pressure slows down decomposition reaction (R3) since the latter is in the falloff region [18]. However, the ratio  $r$  can still remain the same, for a given initial concentration of aromatic hydrocarbon, if the temperature is raised to compensate for the reduction in pressure. Thus, the soot yield "bell" is shifted toward higher temperatures as the total pressure is decreased. The width of the "bell" is slightly increased because increasing the temperature also enhances the polymerization along with the decomposition. The extent of the shift depends on the total pressure itself, according to the falloff behavior of the decomposition that can account for the much smaller pressure effect observed at higher pressures [6].

It was mentioned in the introduction that opposite dependences on the initial concentrations of the parent aromatic hydrocarbon were observed by Wang et al. [6] and Vaughn [11]. This fact cannot be explained within the framework of simple reactions (R3) and (R4) since, as was discussed earlier, varying only the denominator of the ratio  $r$  produces a monotonic function of the yield of  $S$ . Introduction, however, of a positive feedback from process (R4) to process (R3) will result in a bell-shaped dependence of the yield of  $S$  versus the initial concentration of  $A$ . The feedback can be visualized, for example, as catalytic decomposition of  $A$  by the side products of the chain process, or as removal of active chain carriers by side reactions, or simply as accumulation of "nonsooting" chain intermediates. The possibilities seem conceivable, and since the concentrations used by Vaughn et al. [10, 11] were higher by an order of magnitude than those employed by Wang et al. [6, 7], both groups were probably studying the opposite sides of the

bell rather than contradictory phenomena. This resolves another apparent paradox in experimental data reported by different investigators.

In the decomposition sequence of toluene, the first step (R1) is much faster than the second step (R2) [18], whereas the time scale of the latter is comparable to that of soot formation. For example, at 1800K and total concentration of  $10^{-2}$  kmol/m<sup>3</sup>,  $1/k_1 \approx 5 \mu\text{s}$ ,  $1/k_2 \approx 200 \mu\text{s}$  [18], and the induction time for soot appearance has the value of hundreds of microseconds (Fig. 7). These considerations suggest that process (R3) of the proposed model might be simulating the fragmentation of the aromatic ring. The assumption is in harmony with the noticed linkage between carbon formation and ring rupture [11, 21]. Then, if  $X$  denotes the fragmentation product, its attack on  $A$  would be concordant with the conclusions of Bittner and Howard [22] and Vaughn [11] on reaction of acetylenelike species with an aromatic ring. Although the chemical nature of such interaction remains unresolved, the fragment attack on the aromatic ring as a vital element in the soot formation process can be postulated. It is still possible, especially at low temperatures, that aromatic radical-ring interaction may be of importance.

The comparison of induction times for soot appearance in the visible and infrared (Fig. 7) may indicate the consecutive character of the soot formation process. Consider an arbitrary sequence



where each step is a first-order reaction with an identical rate constant,  $k$ . The species are distributed according to Poisson distribution [23],

$$[B_i]/[B_0]_0 = (kt)^i e^{-kt}/i! \quad i = 0, 1, 2, \dots,$$

and therefore the expectation of  $i$  is given by

$$E(i) = kt,$$

or, in other words, the concentration of species  $B_i$  reaches a maximum value at time

$$t_i = i/k. \quad (4)$$



Assume that laser absorption is employed as a monitoring technique and that all species  $B_l$ , where  $l = i, i + 1, \dots$ , absorb light at wavelength  $\lambda_i$ . Assume further that a characteristic induction time can be defined as a time at which the concentration of  $B_i$  reaches its maximum, i.e., Eq. (4). Therefore the ratio of the induction times monitored at two different wavelengths  $\lambda_i$  and  $\lambda_j$  is given by

$$t_i/t_j = i/j. \quad (5)$$

Inspection of Eq. (5) indicates that the ratio of the induction times is invariant with temperature (of course, within the limitation of a weak dependence of absorptivity itself on temperature). Analogous results can be obtained for more complex but consecutive sequences because their kinetic behavior is reduced to Poissonlike distributions.

Taking into account that at shorter wavelengths the sensitivity level of absorption shifts towards lower molecular weight intermediates [4], i.e.,  $i > j$  for  $\lambda_i > \lambda_j$ , the results presented in Fig. 4 and 7 can be interpreted within a consecutive model. The constant ratio of the induction times (Fig. 7) follows from expression (5). An increase in the wavelength of the absorption actually increases the time scale of polymerization in the conceptual model, which explains the shift of soot yield maxima toward higher temperatures in the infrared mode (Fig. 4).

## CONCLUSIONS

A conceptual model for soot formation during the pyrolysis of aromatic hydrocarbons has been postulated as being a free-radical-polymerization-type process which is initiated by fragmentation of the aromatic ring. The model unifies results and hypotheses of various researchers and provides a starting point for future empirical modeling.

*This work was supported by the Pittsburgh Energy Technology Center of the Department of Energy under the auspices of Grant Number DE-FG22-80PC30247.*

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*Received 23 October 1981; revised 12 April 1982*