The Correlation of Benzene Production with Soot Yield
Determined from Fuel Pyrolyses


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Introduction

The rate of production of soot in pyrolytic reaction systems has been studied in shock tubes using a variety of non-intrusive analytical techniques; laser extinction (LEX)\(^1-6\), static analysis of the product distribution from single pulse shock tubes (SPST)\(^7-9\), and dynamic analysis of the reflected shock zone by time-of-flight mass spectrometry (TOF)\(^10\). The data reduction process often involves measurement of a changing bulk quantity; e.g., attenuation of a He-Ne laser beam due to absorption by high molecular weight gas phase species and discrete soot particles via LEX or deficiencies in the carbon atom mass balance via SPST or TOF. The concentrations of the various polycyclic hydrocarbons formed in the pre-particle soot chemistry phase are extremely low\(^9\) and are below the detectability limit of the TOF technique\(^10\) which is about \(10^{-10}\) mol cm\(^{-3}\). The non-detected hydrocarbons constitute the "missing" mass.

The ultimate goal of the work in this area is to write a complete chemical mechanism for soot formation. This formidable task has been attempted for acetylene\(^11\). Some 180 species and 600 reactions were considered in an effort to model the soot yield obtained by LEX. Both the calculated and experimental yields were very low (\(<\) 1%). Comparison of the calculated results with the measured bulk quantity was obtained by assuming that all species in the model having \(MW>300\) absorbed 632.8 nm radiation. The summation of these high molecular weight concentrations converted to carbon atoms cm\(^{-3}\) and divided by the input carbon atom concentration yielded the computed soot yield.

The effort herein is to develop a correlation between a readily observable molecular species whose presence is diagnostic of subsequent soot formation and the bulk observables of laser extinction and mass balance deficiency.

Experimental Techniques Employed

LEX has been utilized behind incident and reflected shock waves during various observation times ranging from 0.5-2.5 ms\(^1-6\). In order to compare the relative sooting tendencies of fuels, a total carbon atom concentration of \(2\times10^{17}\) atoms cm\(^{-3}\) was chosen for such fuels as ethylbenzene, toluene, benzene, pyridine, allene, 1,3 butadiene, vinylacetylene, and acetylene. The soot yield vs the no-reaction shock zone temperature curves are bell-shaped. Aromatic compounds produced the greatest amount of beam attenuation or soot yield while
acetylene exhibited the least. The early LEX work\textsuperscript{1–3} reported values for the absolute soot yield on the order of 80 – 90\% conversion of aromatic fuels to soot. It was subsequently realized that these values were too high due in part to uncertainty of the literature value for the refractive index of soot and to light absorption by pre-particle species.\textsuperscript{4} It was also known that a significant amount of soot formation occurred in the accompanying cooling wave.\textsuperscript{7,8} For these and other reasons, the ordinate for soot yield plots was taken to be $E(m) \times $ soot yield with the value of $E(m)$ left unspecified pending resolution of the uncertainties.\textsuperscript{4,5} This adjustment cast the LEX results as a measurement of relative rather than absolute soot yields.

The thrust of the mass balance deficiency procedure was to add up all of the carbon containing products detected and subtract from the total carbon atoms in the original fuel. Aromatic compounds showed the greatest deficiencies (with the notable exception of pyridine\textsuperscript{6}) and acetylene the least. There was good agreement with regard to the relative sooting tendencies of fuels investigated with LEX and the mass deficiencies obtained by SPST and TOF.

The TOF method offers the advantage of recording the product distribution at selected times during the reaction. Concentration profiles of various observed species are constructed within the m/e range of 12 – 300 during typical observation times of $\sim 0.75$ ms. The data are fit with computed lines from proposed or known mechanisms. Benzene has been recorded during the pyrolyses of allene\textsuperscript{12}, 1,2 butadiene\textsuperscript{13}, and 1,3 butadiene\textsuperscript{14}. The profiles have been modeled using the CHEMKIN program\textsuperscript{15,16} with reasonable success.

\textbf{Results and Discussion}

In order to mimic the soot bells determined by LEX, benzene concentrations were modeled for the thermal decompositions of C$_3$H$_4$\textsuperscript{12}, 1,2 C$_4$H$_6$\textsuperscript{13}, 1,3 C$_4$H$_6$\textsuperscript{14}, C$_4$H$_4$\textsuperscript{17}, C$_5$H$_5$\textsuperscript{18}, and C$_2$H$_2$\textsuperscript{19}. In each of these pyrolyses investigated by the TOF method, the total carbon atom concentration was approximately $2 \times 10^{17}$ atoms cm$^{-3}$. The benzene concentrations were calculated for each of these fuels at 1 ms as a function of no-reaction shock temperature in order to compare with the LEX work. The TOF and LEX results are shown in Figures 1 and 2. Before discussing each fuel individually, we note that the benzene concentration curves are bell shaped, that the relative amounts of benzene formed are in the same general order as the sooting tendencies, and that the benzene maximum for each fuel precedes the respective soot tendency maxima.

\textbf{Allene}

A 4.3\% C$_3$H$_4$–Ne mixture was investigated over the temperature and total pressure range of 1300–2000 K and 0.2–0.5 atm, respectively. TOF analysis revealed that the major products were C$_2$H$_2$, C$_4$H$_2$, CH$_4$ and C$_6$H$_6$; lesser amounts of C$_2$H$_4$, C$_2$H$_6$, C$_4$H$_4$, and C$_6$H$_2$ were detected. The major product profiles were modeled with an 80 step reaction mechanism. The initial reactions involved the isomerization of allene to propyne\textsuperscript{20}; both isomers decompose to yield C$_3$H$_3$ + H\textsuperscript{21,22}. Benzene was produced via reaction of C$_3$H$_3$ with allene and by reaction of

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two C\textsubscript{3}H\textsubscript{3} radicals. The latter route was suggested by Hurd\textsuperscript{23,24} in which C\textsubscript{3}H\textsubscript{3} initially forms :CH=CH-\textsuperscript{2}CH=CH via 1,2 H shift followed by cyclization to benzene. Benzene concentrations were calculated at 1 ms for various no-reaction temperatures. The resulting bell shaped curve is displayed in Figure 1 along with its respective LEX soot tendency bell\textsuperscript{5}.

1,2 Butadiene

A 3\% 1,2 C\textsubscript{4}H\textsubscript{6}-Ne mixture was shocked over the ranges 1200-2000 K and 0.17-0.56 atm. The major stable species observed were C\textsubscript{2}H\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{4}H\textsubscript{2}. At intermediate temperatures (around 1500 K), benzene and toluene were recorded. C\textsubscript{2}H\textsubscript{2} and C\textsubscript{4}H\textsubscript{2} were the only major products at high temperatures. Isomerization of 1,2 to 1,3 C\textsubscript{4}H\textsubscript{6} precedes extensive decomposition. The two isomers decompose according to two pathways.

\begin{align*}
1,2 \text{C}_4\text{H}_6 & \rightarrow \text{CH}_3 + \text{C}_3\text{H}_3 \quad 1) \\
1,3 \text{C}_4\text{H}_6 & \rightarrow 2 \text{C}_2\text{H}_3 \quad 2)
\end{align*}

The decomposition of 1,3 C\textsubscript{4}H\textsubscript{6} has been studied by laser schlieren densitometry (LS) and TOF\textsuperscript{14}. The reaction mechanism used to model the various product profiles from 1,3 C\textsubscript{4}H\textsubscript{6} was employed as a subset to the mechanism for 1,2 C\textsubscript{4}H\textsubscript{6}. Reactions describing the isomerization and other key channels complete the model. Benzene concentrations were calculated at 1 ms and are plotted as a function of temperature in Figure 1. There are no LEX data available for comparison.

1,3 Butadiene

A 3\% 1,3 C\textsubscript{4}H\textsubscript{6}-Ne mixture was studied over the range comparable to 1,2 C\textsubscript{4}H\textsubscript{6}. LS profiles obtained by Professor Kiefer provided conclusive evidence that the main pathway for decomposition was C-C bond rupture to produce two vinyl radicals. A 31 step mechanism modeled the LS profiles and the TOF profiles for 1,3 C\textsubscript{4}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{4}H\textsubscript{2} and C\textsubscript{6}H\textsubscript{6}\textsuperscript{14}. The amount of benzene produced was less than that recorded for 1,2 C\textsubscript{4}H\textsubscript{6} and for an equivalent amount of C\textsubscript{3}H\textsubscript{3}. The latter result is in agreement with the LEX work\textsuperscript{5} which is shown in Figure 1.

Acetylene

C\textsubscript{2}H\textsubscript{2} is the major product in the high temperature thermal decompositions of many hydrocarbons; C\textsubscript{8}H\textsubscript{10}\textsuperscript{25}, C\textsubscript{7}H\textsubscript{8}\textsuperscript{26}, C\textsubscript{6}H\textsubscript{6}\textsubscript{27-29}, C\textsubscript{5}H\textsubscript{10}\textsuperscript{18}, C\textsubscript{3}H\textsubscript{4}\textsubscript{12}, 1,2\textsubscript{12} and 1,3 C\textsubscript{4}H\textsubscript{6}\textsuperscript{14}, and C\textsubscript{4}H\textsubscript{4}\textsuperscript{30}. A radical mechanism derived largely from those previously employed by Gardiner\textsuperscript{31} and Kiefer\textsuperscript{32} was used to model TOF data obtained on a series of C\textsubscript{2}H\textsubscript{2}-Ne mixtures, 1-6.2\%, over the range 1900-2500 K and 0.3-0.55 atm. The major species modeled were C\textsubscript{2}H\textsubscript{2}, C\textsubscript{4}H\textsubscript{2}, and C\textsubscript{6}H\textsubscript{2}. Minor amounts of C\textsubscript{8}H\textsubscript{2} and C\textsubscript{4}H\textsubscript{3} were recorded; benzene was not detected. Reactions from the benzene mechanism\textsuperscript{29} were added to the model and used to calculate the relatively minor amounts of benzene detected in the SPST work by Colket\textsuperscript{5}. The results are shown in Figure 3. Although the fit is not completely satisfying, the computed profile is satisfactory for our purpose here; namely, the benzene yield is very low compared to the major species present. Benzene concentrations for an acetylene
mixture containing $2 \times 10^{17}$ C atoms cm$^{-3}$ are plotted in Figure 2 along with the corresponding LEX soot bell$^5$.

**Vinylacetylene**

Pyrolysis of C$_4$H$_4$ has been studied recently by LS and TOF over the range 1500-2500 K and 0.14-0.56 atm$^3$. Analysis of the LS profiles revealed that the decomposition was characterized by a heat release of $\sim 40$ kcal mol$^{-1}$. The LS profiles were all concave upward which ruled out any appreciable chain acceleration reactions. TOF measurements of the major products, C$_2$H$_2$ and C$_4$H$_2$ disclosed a near constant ratio of C$_2$H$_2$/$C_4$H$_2$ $\sim 5$ which was independent of the observation time and temperature. Trace amounts of C$_6$H$_2$ were recorded at higher temperatures; C$_8$H$_2$ and benzene were not detected. These facts support the proposal that the mechanism is molecular and occurs via the reactions

$$C_4H_4 + M \rightarrow 2C_2H_2 + M \quad 3)$$
$$C_4H_4 + M \rightarrow C_4H_2 + H_2 + M \quad 4)$$

The LS profiles and the TOF profiles were fit with rate constants derived for this two channel dissociation. These conclusions are in conflict with two other shock tube reports that propose a radical mechanism for the pyrolysis in which the first step is C-H bond rupture$^{33,34}$.

$$C_4H_4 \rightarrow C_4H_3 + H \quad 5)$$

The initiation is followed by a sequence of radical reactions. The benzene concentrations shown in Figure 2 were calculated using rxs 3) and 4) along with the C$_2$H$_2$$^{19}$ and C$_6$H$_6$$^{29}$ mechanisms previously mentioned to fit the SPST data in Figure 3.

**Pyridine**

LS and TOF profiles have been recently obtained$^{18}$ for the thermal decomposition of C$_5$H$_5$N over the range 1700-2200 K and 0.13-0.5 atm. The LS profiles displayed local maxima which is a signature for chain acceleration of the net endothermic rate. The main products were identified by TOF to be HCN, C$_2$H$_2$, and C$_4$H$_2$. A 24 step mechanism was constructed which included the following steps:

$$C_5H_5N + M \rightarrow C_5H_4N + H + M \quad 6)$$
$$H + C_5H_5N \rightarrow C_5H_4N + H_2 \quad 7)$$
$$C_5H_4N + M \rightarrow C_5H_3 + HCN \quad 8)$$

Benzene concentrations were calculated in the manner employed for C$_4$H$_4$ and are extremely low which is in accord with the LEX result$^6$. The near absence of this key building block inhibits polycyclic growth and subsequent soot formation. Intact pyridine rings are not suitable substitutes since polycyclic growth is retarded by the presence of the ring nitrogen.
Temperature Changes

Thermal decompositions are endothermic processes and the system temperature decreases as the reaction progresses. This point is illustrated in Figure 4 in which the soot bell for toluene at 1 ms observation time is shifted markedly when the system temperature at 1 ms is used to plot the sooting tendency instead of the usual practice which employs the no reaction temperature. The temperatures at 1 ms were calculated using a mechanism from recent LS and TOF work on C7H8 which identifies the major pathway for dissociation as

\[ C_7H_8 + M \rightarrow C_6H_5 + CH_3 + M \]  

Temperature decreases for the pyrolysates represented in Figures 1 and 2 at 1 ms are listed in Table 1.

Conclusions

There appears to be sufficient evidence to support the correlation of benzene production and soot tendencies. It does not necessarily follow that the key to soot control is limiting solely those reactions and/or species which promote benzene formation. The pyrolysates considered herein were those of "pure" fuels. Synergistic effects have been reported for fuel mixtures; e.g., a 0.75% C7H8 - 0.75% C5H5N - Ar mixture produced almost as much soot as an equivalent amount of "pure" toluene, 1.5% C7H8 - Ar. Nevertheless, the results herein are consistent with the proposal of relatively low concentrations of soot nuclei which subsequently increase in mass due to surface growth by C2H2.

Acknowledgments

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References

Table 1.

Temperature Decrease During Pyrolyses of Various Fuels

<table>
<thead>
<tr>
<th>$T_0 (K)$</th>
<th>$-\Delta T$ (1.0 msec, $2 \times 10^{17}$ C atoms cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_3H_4$</td>
</tr>
<tr>
<td>1500</td>
<td>-</td>
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<td>2300</td>
<td>258</td>
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<tr>
<td>2400</td>
<td>264</td>
</tr>
</tbody>
</table>
Figure 2

% SOOT YIELD x E(M)

TEMP, K

log [C6H6] mol cm⁻³

C₂H₂, C₂H₄, C₄H₄, C₅H₅N
Figure 4

The figure shows a graph with the x-axis labeled "TEMP., K" and the y-axis labeled "% SOOT YIELD \times E(m)". Two curves are plotted on the graph: one dashed curve marked "T_{1.0} \text{ msec}" and one solid curve marked "T_0". The graph illustrates the relationship between temperature and soot yield over a range of temperatures from 1400 K to 2400 K.