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Evidence for the contribution of methane in the formation of aromatics and soot in fuel-rich pre-mixed combustion

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Abstract

Experimental results from an isothermal laminar flow reactor at atmospheric pressure are presented on the chemical composition in the post-oxidative region of two sooting fuel-rich pre-mixed mixtures diluted in nitrogen. A base case composed of *n*-heptane and O_2 in N_2 at 1425 K with a C/O of 2.85 was perturbed by substituting 10% of the carbon in *n*-heptane with carbon as CH₄. While these changes would intuitively reduce aromatics and soot formation by increasing H₂ and decreasing C₂H₂ concentrations, we observe the opposite. The concentrations of individual aromatic species are observed to actually increase by up to 50% and the soot yield increases by 80%. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Past experimental evidence has shown that acetylene and molecular hydrogen are controlling elements in the reaction bath for polycyclic aromatic hydrocarbon (PAH) growth in fuel-rich pre-mixed combustion (Bockhorn, 1994). According to the HACA, polymeric growth sequence model suggested by Frenklach et al. (1984), acetylene is the carbon-addition element and molecular hydrogen is a species that tends to reduce the growth process by competing for radical sites. Methane is also an important product in fuel-rich combustion systems whose role in the growth process of high molecular weight compounds has not been addressed in much detail as it is the least sooting hydrocarbon. Furthermore, Harris and Weiner (1983) have argued that methane cannot be an important soot growth species in pre-mixed atmospheric pressure flames. The present work provides new insight into the action of methane by showing that its presence in the soot growth environment contributes to the growth rate of aromatic soot pre-cursor compounds.

2. Experimental set-up

The experiments are performed in an isothermal laminar non-plug-flow reactor operating at atmospheric pressures in a three-zone temperature controlled furnace described elsewhere (Roesler, 1998; Roesler and Auphan-de-Tessan, 1998). Following rapid heat-up, the 98% nitrogen diluted pre-mixed reactants enter a 3 cm diameter quartz duct and the flow is laminarized by passing through a porous quartz disk prior to entering the 30 cm test section. The temperature profile measured under a flow of nitrogen is flat within 5 K. A fraction of the combustion products (20%) are sampled along the center-line axis and quenched by an oil-cooled probe at 200°C. Soot is filtered at 200°C and condensable species are then trapped. In a first pass, the trap is at ambient temperature and the low molecular weight gas phase species, up to benzene, are analyzed on line with a FTIR spectrometer. The higher molecular weight species are

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collected on a second pass with the trap at dry-ice temperature (-70° C). All wetted surfaces (probe Teflon liner, soot filter and cold trap) are washed ultrasonically with CH₂Cl₂. The detailed speciation of the CH₂Cl₂ soluble fraction is obtained by GC–FID and GC–MS analysis. The total masses of condensable species (CS) of molecular weight species greater than acenaphthylene and the mass of soot (non-dichloromethane-soluble condensable species) are determined gravimetrically.

3. Results and discussion

In order to bear some relation to a diesel fuel, the initially injected hydrocarbon is *n*-heptane. Its purpose is primarily to generate a C_2H_2 -H₂ (and now CH₄) bath for PAH and soot formation. Two mixtures are studied at 1425 K with a bulk mean flow velocity of 61 cm/s. The first, BATH1 contains initial mole fractions of 0.49% *n*-heptane and 0.6% O₂ yielding an equivalence ratio of 9.0 and a C/O ratio of 2.85. BATH2 has the same total carbon content and C/O ratio, but 10% of the carbon is injected as methane instead of *n*-heptane.

Fig. 1 displays the measured species profiles. The decomposition of *n*-heptane is not observed in these experiments because it occurs in the pre-heat region on a time scale that is much shorter than that of PAH and soot formation. The oxygen is also consumed rapidly in the pre-heat region. The profiles of CO, H_2O and CO_2 are thus nearly flat. The molecular hydrogen content is obtained by H-atom balancing on the measured species and on the amount of injected *n*-heptane. Other species would contribute negligibly. The rise in molecular hydrogen along the reactor tube results from the decay of ethylene, methane and acetylene that are the three main hydrocarbon species remaining at the end of the preheat zone.

The effect of changing the initial mixture composition on the growth bath composition is only to alter methane and acetylene concentrations. Methane is relatively slow to oxidize and its addition yields a 70% self-increase in BATH2 relative to BATH1. In contrast, the acetylene concentration is reduced by 20% due to the reduction in initial *n*-heptane. The global effect is therefore a substitution of C_2H_2 with methane in equal carbon proportions.

Based on the reaction systems described above one would intuitively argue that, with less C_2H_2 and equal H_2 concentrations, the formation of benzene, PAH and soot should be reduced. Yet the experimental data indicate just the opposite: the rate of formation of C_6H_6 increases by 60%. The concentrations of the PAH and soot have been measured only at the 20 cm position and increase in relative amounts that are species-dependent. Naphthalene increases from 11 to 16 ppmv (+45%), acenaphthylene from 13 to 16 ppmv (+23%), fluoranthene from 1.3 to 1.5 ppmv (+15%), pyrene from 2.1 to 3.2 ppmv (+50%), CS from 0.29 to 0.33 mg/l in the hot gases (+15%), and soot from 0.048 to 0.084 mg/l of soot (+80%). The later increase is likely to be the cumulated effect of a shortened induction period and faster growth rate. Thus, globally the effect of the added methane extends throughout the total chain of reactions leading to soot.

These results concur with recent experiments that showed a methane laminar pre-mixed flame to produce more PAH than an equivalent C_2H_6 flame (Senkan and Castaldi, 1996). While the flame data provide a global difference between the two fuel types in a complex reaction system with large temperature gradient, the present results isolate the specific role of methane by imposing only a perturbation in an isothermal reaction bath. Senkan and Castaldi (1996) suggested that the presence of methyl radicals promotes the formation of



Fig. 1. Mole fraction profiles measured along the reactor axis. Dashed lines and open symbols are curve fits and data for BATH1 (no added methane). Solid lines and filled symbols are curve fits and data for BATH2 (added methane).



Fig. 2. Calculated species profiles using the detailed reaction mechanism of Marinov et al. (1996) to show that the observed experimental effects are qualitatively reproduced. Calculations were performed assuming plug-flow conditions. BATH1 (no added methane): dashed lines, BATH2 (added methane): solid lines.

hydrocarbon species containing an odd-number of carbon atoms, which would then accelerate benzene and naphthalene production via mechanisms proposed by Marinov et al. (1996, 1997, 1998). Accordingly, a possible mechanistic interpretation is that methane increases the methyl radical concentration and subsequently the following chain of reactions that lead to benzene:

$$CH_3 + C_2H_2 \rightarrow pC_3H_4 (propyne) + H$$
 (1)

$$pC_3H_4 + H \rightarrow C_3H_3 (propargyl) + H_2$$
(2)

$$C_3H_3 + C_3H_3 \rightarrow \text{ benzene}$$
 (3)

The additional benzene itself could drive the formation of PAH and soot to higher concentrations via HACA reaction steps (these involve even-carbon numbered species), or other pathways involving methyl radicals and odd-carbon numbered species may be involved such as the formation of naphthalene via:

$$C_2H_4 + CH_3 \rightarrow C_3H_6 + H \tag{4}$$

$$C_2H_3 + CH_3 \rightarrow C_3H_6 \tag{5}$$

$$C_3H_6 \rightarrow 1\text{-}C_3H_5 + H \tag{6}$$

$$1-C_3H_5 + C_2H_2 \rightarrow cC_5H_5 \text{ (cyclopentadienyl)} + H \qquad (7)$$

$$cC_5H_5+cC_5H_5\rightarrow C_{10}H_8 \ (naphthalene)+H+H \ \ (8)$$

Calculations performed with the detailed kinetic reaction mechanisms of Marinov et al. (1997) are qualitatively capable of predicting the observed effects as shown in Fig. 2: adding methane accelerates the growth of aromatics. The calculations were performed using an isothermal plug-flow reactor approximation with initial conditions given by the measurements at the 10 cm position as given in Fig. 1. All other species concentrations, including benzene, were initially set to zero. Calculations with the Wang and Frenklach (1997) reaction mechanism gave poorer predictions with still a 30% rise in benzene growth rate but with decreases in naphthalene and pyrene. The later mechanism includes benzene production via reaction (3), but does not include growth of PAH via odd-carbon numbered species, which is likely to explain its poorer trends predictions.

In conclusion, our experimental results demonstrate that methane contributes significantly in determining the growth rate of aromatic species and soot in fuelrich pre-mixed combustion. Detailed modeling of combustion chemistry is sufficiently well developed that it can qualitatively predict the present observations. These models will help identify the implications of the findings on PAH and soot formation in practical combustion devices. More detailed experimental and modeling work is under way to provide deeper insights into the chemical role of methane identified here.

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