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Introduction: The formation of aromatics and PAH's is an important problem in combustion. These compounds are believed to contribute to the formation of soot whose emission from diesel engines is regulated widely throughout the industrial world. Additionally, the United States Environmental Protection Agency regulates the emission of many aromatics and PAH species from stationary industrial burners, under the 1990 Clean Air Act Amendments. The above emission regulations have created much interest in understanding how these species are formed in combustion systems.

Much previous work has been done on aromatics and PAH's. The work is too extensive to review here, but is reviewed in Reference 1. A few recent developments are highlighted here. McEnally, Pfefferle and coworkers have studied aromatic, PAH and soot formation in a variety of non-premixed flames with hydrocarbon additives [2-4]. They found additives that contain a C5 ring increase the concentration of aromatics and soot [4]. Howard and coworkers have studied the formation of aromatic and PAH's in low pressure, premixed, laminar hydrocarbon flames. They found the cyclopentadienyl radical to be a key species in naphthalene formation in a fuel-rich, benzene/Ar/O2 flame [5].

Approach: The detailed reaction mechanism for aromatic and PAH formation was initially developed using the work of Miller and Melius, Tsang, Pitz and Westbrook, Emdee, Brezinsky and Glassman, Marinov and Malte, and Wang and Frenklach [5-11]. Experimental data [1,12-15] from laminar premixed and diffusion flames were used to develop a detailed chemical kinetic model. Thermodynamic data was obtained from the literature and when not available, Benson group additivity methods and electronic structure calculations have been used to obtain thermodynamic parameters for stable and radical species. Electronic structure calculations have also been used to obtain the entropy and enthalpy of transition states. This information was used to estimate reaction rates using transition state theory for selected reactions. Reaction rate parameters were obtained from the literature and by analogy to similar reactions. Quantum Kassel and RRKM theory has been used to obtain the pressure and temperature dependence of selected reactions and their various product channels.

Results: One of the main themes of this work is the role of resonantly-stabilized radicals in forming aromatics and PAH's. Modeling results have identified two paths as being important in the formation of benzene in fuel-rich premixed flames and diffusion flames, both of which involve resonantly stabilized radicals. The paths are illustrated in Fig. 1. They involve the reaction of allyl and propargyl radicals and the self-reaction of propargyl radicals. The self-reaction of propargyl radicals to form benzene has been investigated by Miller and Melius [6]. This reaction was found to play a major role in methane, ethane, ethene, propane and n-butane, fuel-rich, premixed flames and in a methane, opposed-flow diffusion flame [1,12-15]. Propargyl is formed by the sequential dehydrogenation of allyl radicals and of propyne. The second path found to form benzene is the reaction of propargyl radical with allyl radicals. The mechanism of the reaction was investigated in Reference 13. In this reaction, the allyl and propargyl radicals combine to form an adduct. The key feature of this reaction is that the allene-like carbon on the propargyl moiety on the adduct adds to the terminal carbon on the allyl moiety. This feature is repeated again in one of the primary reactions forming naphthalene discussed later. After the above addition step, a hydrogen atom shifts and eliminates to form fulvene. Fulvene isomerizes rapidly to benzene [16]. The reaction of propargyl and allyl radicals was found to be one of the most important paths forming benzene in a methane, opposed-flow diffusion flame and produced 20 to 30 percent of the benzene in propane and n-butane, rich, premixed flames [13-15].

The theme of the importance of the reaction of resonantly-stabilized radical continues with the formation of naphthalene. Modeling results indicate that the main paths to naphthalene involve resonantly stabilized radicals. The two main paths identified were the reaction of benzyl and propargyl radicals and the self-reaction of cyclopentadienyl radicals. The reaction of benzyl and propargyl radicals [15] (Fig. 2) follows a similar reaction mechanism as the allyl + propargyl reaction. After allyl and propargyl radicals combine to form an adduct, the allene-like carbon on the propargyl moiety adds to the benzene ring. Subsequently, the H-atom on the tertiary carbon is very weak (24 kcal/mole) and is eliminated (dashed line). With an H-atom elimination of a secondary H-atom, the fulvene moiety is formed. As seen in the analogous reaction forming benzene, the fulvene ring isomerizes rapidly to a benzene ring and naphthalene is formed. The benzyl + propargyl reaction was found to be the main reaction forming naphthalene in the methane, opposed-flow diffusion flame. The second path found to be important in forming naphthalene is the self-combination of cyclopentadienyl radicals. The mechanism of this path was first described by Melius et al. [16]. This path was found to be important in rich, premixed methane , ethane, propane, n-butane flames [1,13,14], but not a major contributor in a methane, opposed-flow diffusion flame [15]. However, the earlier modeling studies of the premixed laminar flames did not include our current treatment of the competing reaction, benzyl + propargyl, to form naphthalene. For the hydrocarbon flames we studied, calculations indicated that hydrogen-abstraction, acetylene-addition paths did not play a major role in the formation of naphthalene [12].

Comparison to Experimental Data: Experimental data was essential to the development of a detailed chemical kinetic model. Species profiles computed by detailed chemical kinetic model were compared to experimental results from methane, ethene, ethane, propane, n-butane, premixed, burner-stabilized flames, and a methane, opposed-flow diffusion flames [1,12-15]. The comparisons are too lengthy to show here. New reaction paths added and reaction rate constants were adjusted based on these comparisons.

The detailed chemical kinetic model was used to simulate the formation of aromatics and PAH's in an industrial burner as part of a joint industrial, national laboratory and university project [17]. A perfectly-stirred reactor (PSR) model was used as a representation of a highly-turbulent reaction zone of a typical industrial burner diffusion flame. The model was used to simulate the emission of aromatics and PAH's as equivalence ratio is varied. The temperature in the PSR was assumed to be 1500 K which was a typical, average temperature found downstream of a full-scale industrial-type burner located at Sandia National Laboratories [17]. The fuel composition was chosen to match the simulated refinery fuel gas used in the experiments: 16.0 percent hydrogen, 7.3 percent propane, 76.7 percent simulated natural gas. The residence time of 10 ms was taken to yield the approximate experimentally-observed benzene concentration in the exhaust gas. The results are shown in Fig. 3. One hundred percent theoretical air is defined as stoichiometric and values below 100 indicate fuel-rich mixtures. The model reproduces the qualitative behavior of the benzene and toluene on the fuel-rich stoichiometries. The model shows the ethyl benzene and xylene to be produced in much lower concentrations, consistent with the experiments. This comparison illustrates that detailed chemical kinetic models can be very useful in interpreting experimental data from practical combustion systems.

Conclusion: The reaction of resonantly-stabilized radicals are found to play an important role in the formation of aromatics and PAH's in laminar premixed and diffusion flames.

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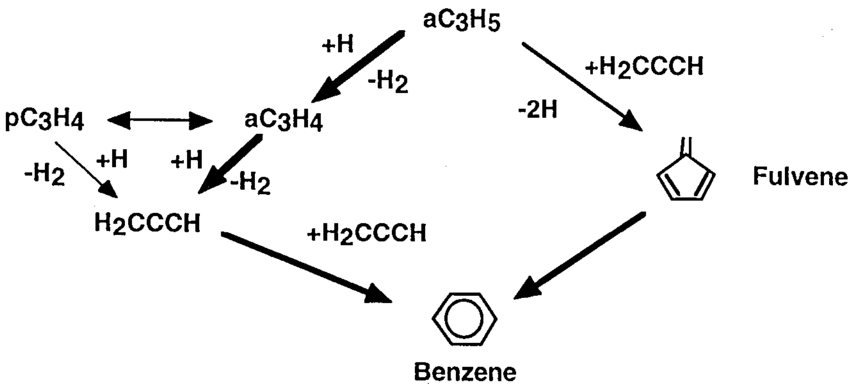

Fig. 1. Reaction paths leading to benzene in a methane, opposed-flow diffusion flame.

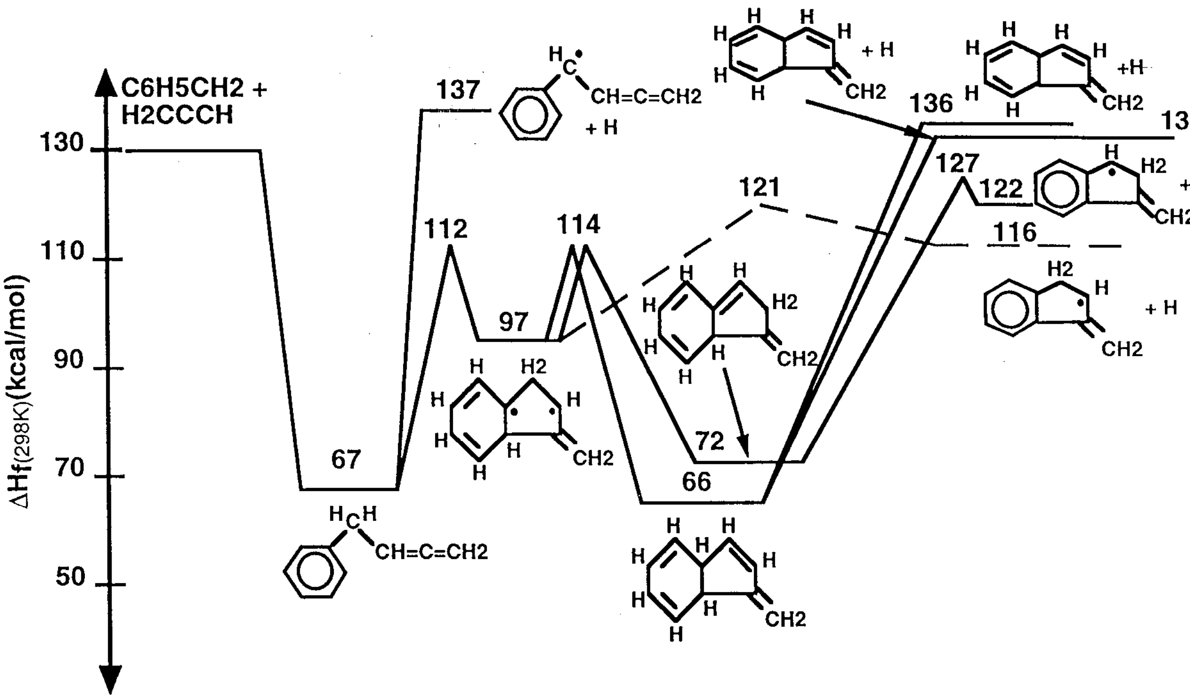

Fig. 2. Reaction coordinate diagram of the reaction of benzyl and propargyl radicals leading to naphthalene.

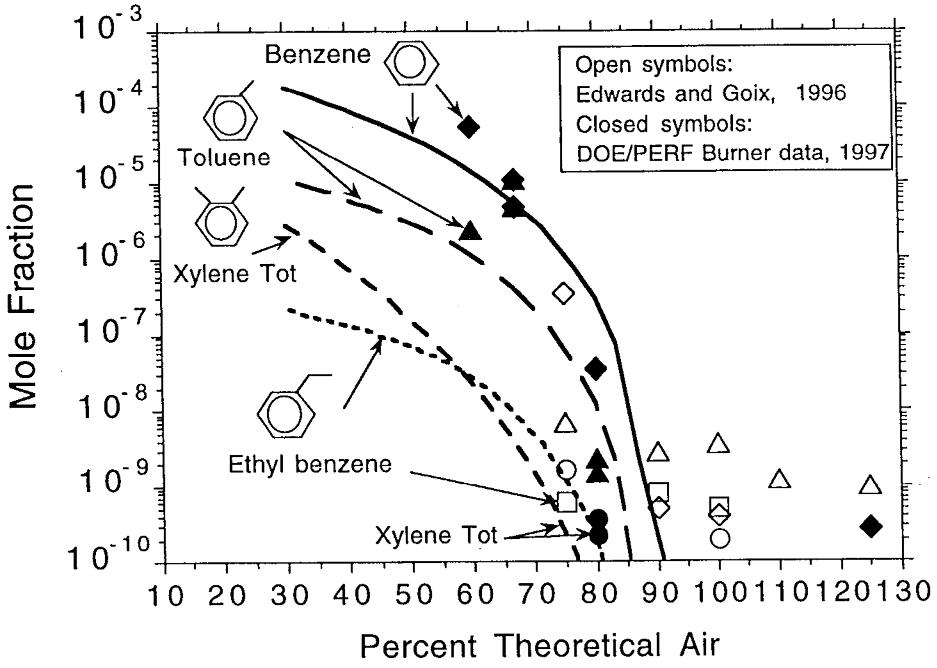

Fig. 3. Comparison between detailed chemical kinetic modeling results from a perfectly stirred reactor (PSR) and full-scale [17] and laboratory-scale emissions [18] from a industrial-type burner. (PSR conditions: 1500K, 10 ms residence time).