PAH formation in one-dimensional premixed fuel-rich atmospheric pressure ethylbenzene and ethyl alcohol flames

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Abstract

This study addresses health-hazardous emissions from combustion of aromatic and oxygenated components of engine fuel blends. An investigation was conducted on the evolution of polycyclic aromatic hydrocarbons (PAH) and other pollutants (soot, CO, unburned light hydrocarbons) emitted from one-dimensional ethylbenzene and ethyl alcohol flames. The study of ethylbenzene combustion is also pertinent to that of waste polystyrene, as past work has indicated that ethylbenzene may be a surrogate for initial products of polystyrene pyrolysis. Both liquid fuels were prevaporized in nitrogen, mixed with oxygen and additional nitrogen, and upon ignition, premixed flat flames were stabilized over a burner. Temperature measurements and product sampling were conducted at various heights above the burner. Results showed that ethyl alcohol combustion generated small yields of PAH, even under the adverse fuel-rich conditions of this study ($\phi = 2.5$). PAH mole fractions in the ethyl alcohol flame were 2–5 orders of magnitude lower than those in the ethylbenzene flame at the same location. PAH mole fractions often peaked in the postflame region and remained at relatively high levels thereafter. PAH mole fractions in premixed fuel-rich benzene, ethane, ethylene, and methane flames, published in the literature, were typically in between those found in the two flames of this study. Computations were conducted using a currently developed detailed kinetic model, allowing for the prediction of formation and depletion of major PAH and soot particles of different sizes. The computed chemical flame structures were compared to experimental data obtained in the present work. Predicted mole fractions were often close to the experimentally obtained values or, at worse, within the same order of magnitude for both fuels. Reaction pathways are discussed.
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1. Introduction

Combustion of the aromatic hydrocarbon ethylbenzene and of the oxygenated aliphatic hydrocarbon ethyl alcohol (ethanol) is of technological interest, as both may be found in commercial fuel blends for engines. Generally, a fuel's content in aromatic and oxygenated components is instrumental both to its combustion characteristics in engines and furnaces and to the emissions of products of incomplete combustion (unburned hydrocarbons, CO, polycyclic aromatic hydrocarbons (PAH) and soot) therefrom; see [1–5]. This work contrasts the emissions of unburned volatile and semivolatile organic compounds (VOC and SVOC) from the combustion of ethylbenzene and ethyl alcohol. Results are interpreted with the help of a chemical kinetic model.

1.1. Ethylbenzene

Aromatics are desirable in gasoline since they increase the octane number. Ethylbenzene is present in gasoline blends with weight fractions in the order of 2% [6]; it is also present in inks, paints, and insecticides. Moreover, since ethylbenzene (C_8H_{10}) has been reported to convert to styrene (C_8H_8) extensively and extremely fast [7], it may be considered as a surrogate of styrene and then, again, of polystyrene ($C_8H_8)_n$ combustion [8]. Thus, this investigation also relates to past work in this laboratory on the combustion and emissions of waste polystyrene (PS), as discussed in the following. PS is the second most common commercial polymer and accounts for 22 wt% of plastics [9]. Presumably because of its aromatic ring structure [10], combustion of PS produces large amounts of soot and polycyclic aromatic hydrocarbons; the equivalent of as much as 25 and 4% of its mass, respectively [11,12]. Past work on combustion behavior and emissions of polystyrene (hydrocarbons, soot, NO_x, CO, and CO_2) has been conducted in this laboratory by burning either single particles or streams of particles in drop tube furnaces [11–18], or by burning fixed beds of polymer pellets in horizontal muffle furnaces [19–24]. The combustion and pyrolysis of polystyrene have also been investigated elsewhere and results have been summarized in [19]. Techniques that minimize emissions of pollutants from PS have been successfully explored in this laboratory [18–24]. However, under conditions often encountered in practical systems, PAH species and soot are generated and once they form they are difficult to destroy [19,21,22]; the mole fraction of some species may even increase in postflame gases. This illustrates the need for identification of operating conditions that minimize pollutant formation and for understanding the underlying chem-

ical processes. To elucidate mechanistic details of PAH formation/oxidation in PS flames and their conversion to soot well-defined experiments are needed, assisted by kinetic modeling. Well-defined conditions may be achieved by combustion of liquid or, better yet, gaseous compounds, thereby avoiding the complex coupling of physical and chemical phenomena of solid fuels, such as PS. Westblad et al. [24] burned batches of liquid styrene under transient conditions, as styrene monomer is the most prominent pyrolyzate of polystyrene thermal degradation [10,24]. While useful conclusions were obtained from that study, theoretical understanding of the involved processes was hampered by the unsteady, unpredictable, and often explosive combustion behavior of styrene. However, using vaporized ethylbenzene as a surrogate of styrene, stable, well-defined flames may be obtained. Thus, to provide data suitable for quantitative understanding, this study burned vapors of ethylbenzene, premixed with oxygen, in steady one-dimensional flames.

Emissions from combustion of ethylbenzene in premixed and diffusion flames have been addressed in a rather limited number of previous studies, including those of Gomez et al. [25], Litzinger et al. [26], Olsen and Pickens [27], McEnally and Pfefferle [28], and Anderson et al. [29]. Litzinger et al. [26] reported on the atmospheric pressure oxidation of ethylbenzene in a turbulent flow reactor at 1060 K. Their equivalence ratios varied between 0.64 and 1.3 and styrene, toluene, benzene, benzaldehyde, and phenol were the light aromatic species identified, along with aliphatic hydrocarbons. They postulated three reaction pathways for the removal of the ethyl group. The most important path starts with abstraction of a hydrogen atom from the ethyl group and then the resulting phenyl ethyl radicals decompose to form styrene or a phenyl radical. Further reactions of styrene are displacement of the vinyl group by a hydrogen atom or oxidative attack on the vinyl. The next important path was identified to be the displacement of the ethyl group from ethylbenzene. The least important path was identified to be the homolytic cleavage in the ethyl group. But they suggested that the importance of this route will increase with increasing temperature because of the high activation energy of homolysis. McEnally and Pfefferle doped nonpremixed methane flames with ethylbenzene and other single ring aromatics [28]. They monitored naphthalene concentrations in the flame. They proposed three decomposition pathways for ethylbenzene: (1) the carbon–carbon bond in the side chain can break to produce a benzyl radical and a methyl radical. (2) An H atom from the interior carbon atom can be removed to form a methyl benzyl radical by thermal decomposition or by abstraction reactions. The methyl benzyl radical