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FLAME STRUCTURE 2014
8th International Seminar on Flame Structure

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A modeling and experimental study of the combustion of laminar premixed C4-flames: 1,3-butadiene, n-butanol, and blends

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Abstract

The oxidation of 1,3 butadiene/n-butanol flames was studied in a combined modelling and experimental work. The aim of the present study is to provide a detailed chemical kinetic reaction mechanism capable to describe the major pathways for butadiene and butanol oxidation as well as the formation of soot precursors and aromatics. In the present work, detailed data on the chemical composition of three premixed, low- pressure (20-30 torr) flames, with different shares of butanol ranging between 25% to 75% compared to butadiene in 50% argon, was used for validation of an in-house reaction model. Mole fraction profiles of reactants, major products, and intermediates including C3Hx and C4Hx radicals and mono aromatics were measured quantitatively as a function of height above burner surface employing flame-sampled molecular-beam mass spectrometry (MB-MS) utilizing photoionization with tunable vacuum-ultraviolet synchrotron radiation. The predictive capability of the reaction model will be discussed, also referring to pure flames of 1,3 butadiene or n-butanol measured earlier, by a comparison of measured species profiles with predicted ones. In general, a good agreement was found between experimental and modelled results, under the current low-pressure, high-temperature conditions. Reaction flux and sensitivity analysis were used to get more insight into the combustion of the fuel.

Introduction

Studying formation and destruction pathways of soot is in the focus of numeral investigations. The addition of small hydrocarbons (1,3-butadiene) to single-ring aromatics (benzene) are considered as major steps in PAH formation and growth reactions [1-2]. The combustion of butanol has gained much interest as butanol offers a renewable way to serve as an additive to gasoline [3] and, furthermore, is promising a less sooting behavior than hydrocarbons [4].

The objective of the present work is to develop a detailed combustion chemistry model for a combined 1,3-butadiene/ butanol flame, which allows to identify the important pathways for

butadiene and butanol oxidation as well as for formation of aromatic species and their precursors. In particular, the importance of vinyl addition to 1,3-C4H6 and/or C4H4 to benzene formation is studied. This work is motivated by the fact that the interactions of the reactive intermediates from both components in such a fuel blend may have consequences for the overall combustion emission. In particular, this work is concerned with understanding the processes leading to the formation of aromatic species and other regulated hazardous air pollutants, such as aldehydes.

Approach

Detailed kinetic modeling results are compared against flame-sampled molecular- beam mass spectrometry data obtained in three fuel-rich laminar premixed flames [3, 5, 6]. The latest experimental data are obtained by utilizing photoionization by tunable vacuum-ultraviolet synchrotron radiation, which allows for the identification and separation of combustion species by their characteristic ionization energies. Newly detected species shed light on critical steps in the growth mechanism in 1,3-butadiene flames. Species profiles as a function of height above the burner were calculated with the one-dimensional code PREMIX using the experimentally determined flame temperature as input parameters, besides initial mass flow rates and initial concentrations composition of the reactants, and the burner's diameter as further input data.

The chemical kinetic model under development is based on the reaction set used previously [5, 7]. The key features of the updated model are the detailed description of 1,3-C4H6 consumption and an accurate treatment of several reactions involving known benzene precursors. Also, the C3H4 chemistry was critically reviewed and a butanol sub-model added.

Results and discussion

The predictive capability of the reaction model with respect to species profiles of the three different flames will be presented below. Thus, the influence of the fuel itself might become more obvious, in particular with respect to possible interactions in the 1,3 butadiene/n-butanol flame. The comparison between measured and predicted species is given for major species (educts: 1,3-butadiene and/or *n-butanol,* O2, Ar; products: H2, H2O, CO, CO2) and selected intermediates (acetylene (C2H2), ethylene (C2H4) and ethane (C2H6)), including major oxygen-containing intermediates (small aldehydes (CH2O, CH3CHO) and alcohol (C2H5OH) as well as radicals (methyl (CH3), propargyl (C3H3) and allyl (C3H5)) and aromatics (benzene (C6H6), toluene (C7H8), and phenylacetylene (C8H6).

Besides the maximum mole fraction, the profile shapes and peak

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positions are also valuable for testing the quality of the reaction model developed. This comparison provides a comprehensive view of the reaction model's quality and predictive capability, with respect to the combustion chemistry of the fuels considered.

In summary, the predicted mole fraction profiles are at least in satisfactory but mostly in very good agreement with the experimentally observed profiles. Furthermore, the reaction model was analyzed (reaction flux and sensitivity analyses) to investigate the importance of consumption pathways of the educts, for example for butadiene and n- butanol.

Conclusions

A detailed in-house chemical kinetic reaction model was developed able to describe the combustion chemistry of a combined 1,3-butadiene/ butanol flame. The reaction model allows identifying the important pathways for butadiene and butanol oxidation as well as for formation of benzene and its precursors. The chemical kinetic model of the present work is based on a reaction model used earlier to describe the oxidation of 1,3-butadiene, propene and cyclopentene flames. A butanol sub-model was added gathered from Dagaut et al. and adopted to the pressure range of the present investigation.

The structure of 1,3 butadiene/n butanol flames experimentally obtained from flame- sampled molecular-beam mass spectrometry data is compared with flame model predictions, also referring to pure flames of 1,3 butadiene and n butanol measured earlier. The predicted mole fraction profiles for important species in the mass range from m/z=1 (H) to m/z=128 (naphthalene) are mostly in very good agreement with the experimentally observed profiles thus allowing an assessment of the importance of various fuel consumption and benzene formation pathways by using reaction flux and sensitivity analyses.

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